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SOME REACTIONS OF DIBENZIODOLIUM SALTS

BY

J.W. GREIDANUS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "SOME REACTIONS OF DIBENZIODOLIUM SALTS", submitted by J.W. GREIDANUS in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Additional evidence for the formation of radicals in the decomposition of certain iodonium compounds in solution is presented.

The reported failure to prepare 2-iodo-2'-methoxybiphenyl from dibenziodolium sulphate and methoxide anion can be explained by dehydrogenation of the solvent methanol. The formation of formaldehyde in this reaction has been demonstrated. When the reaction is carried out in t-butyl alcohol with sodium t-butoxide the corresponding t-butoxy ether is formed.

A tentative explanation for the difference in the behaviour of diphenyliodonium and dibenziodolium cation with respect to methoxide anion and for the identical behaviour of these cations with respect to the anion of dimedone is given. The formation of an intermediate covalent dimedate is suggested.

The preparation of some new dibenziodolium salts is described. A hydroxide — the first pure solid iodonium hydroxide that is reported —, a dimedate and a barbiturate have been isolated as colourless mono- or dihydrates which can be converted very easily into yellow anhydrous compounds. The yellow 2-phenyldimedate and the 2-naphthalenethiolate are described.

The decomposition of the latter in cyclohexane, carbon tetrachloride, and tetrahydrofuran has been studied. The products indicate that a radical mechanism is operating. The results in combination with spectral studies of dibenziodolium 2-naphthalenethiolate have led to the conclusion that the iodine-sulphur bond in this compound is covalent and not ionic.

An attempt to prepare and isolate 5-phenyldibenzobromole was fruitless.

The iodine analogue, which was known already, and its p-methoxy and p-dimethylamino derivatives have been prepared as well, but the compounds were so unstable that their ultraviolet spectra could not be obtained.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. R. B. Sandin for his enthusiastic guidance and encouragement throughout this work.

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Finally, the author expresses his appreciation to his wife, Janny, for her patience and understanding.

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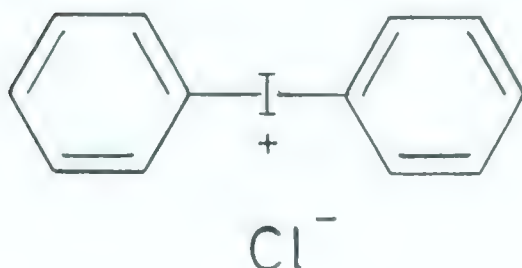
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SECTION 1

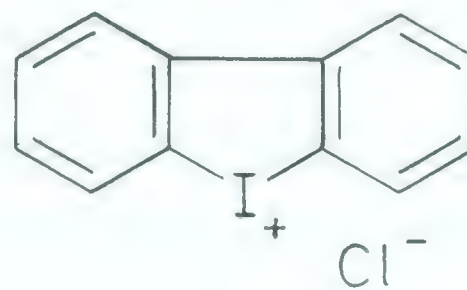
I N T R O D U C T I O N

PREAMBLE

Iodonium salts are derivatives of a hypothetical base H_2IOH and have the general formula $R_2I^+B^-$ in which R represents an aryl group usually. The iodine atom exerts a valence greater than one and these compounds are true representatives of the large class of onium salts.



Diphenyliodonium chloride



Dibenziodolum chloride

(For nomenclature see Appendix)

The decomposition of iodonium salts has been the subject of many studies because it is interesting for several reasons. The thermal decomposition is useful in synthetic work but more recently most attention has been directed at the reaction mechanism of the decomposition.

When the present work was started its object was not the study of one single phenomenon or the synthesis of a specific compound. Its aim was to add to the already existing body of evidence for the occurrence of radical species in reactions of iodonium compounds and, if possible, to prepare aromatic compounds containing tricovalent iodine. The interest taken in the latter was obvious because they were expected to be precursors in the formation of radical intermediates.

Two triaryliodines had been prepared by Wittig and Clauss (1, 2, 3) and it seemed interesting to try to prepare a few others and also a bromine analogue. In view of the instability of the two known compounds of this class, an aromatic compound containing tricovalent bromine was expected to be very unstable, if it was formed at all.

A class of iodonium salts on which attention was focused was that of the thiolates. Whenever a reaction between the diphenyliodonium cation and sulphide or thiolate ion occurred a transient yellow colour or occasionally a rapidly decomposing yellow precipitate had been noticed and often there had been evidence for the formation of radical intermediates (4, 5, 6).

When dibenziodolium cations were used instead of diphenyliodonium cations the stability of the thiolate seemed to be slightly greater. Therefor a search was carried out for a relatively stable thiolate. Also other dibenziodolium salts which had interesting properties were synthesized. Partly this was done because of the findings of Fuson and Albright (7) and of Beringer and co-workers (8). The latter had described the preparation of anisole from diphenyliodonium salt and methoxide anion (9). Fuson and Albright in an attempt to prepare 2-iodo-2'-methoxybiphenyl from dibenziodolium sulphate by the same method were unsuccessful and blamed the greater resistance of the cyclic iodonium compound to nucleophilic displacement by methoxide ion for their failure although other products of their reaction were a result of opening of the cyclic iodonium structure. When Beringer and co-workers (8) reported the isolation of the dimedone derivative of formaldehyde after decomposition of a substituted diaryliodonium salt in the presence of the anion of dimedone, an investigation based on these results seemed interesting and was carried out.

In the following literature survey attention will be focused on a possible ionic or free-radical mechanism of the decomposition of iodonium salts.

LITERATURE SURVEY

Lucas and co-workers (10) concluded in 1936 from the fact that only the o-isomer of iodotoluene was formed in the thermal decomposition of di-o-tolyliodonium iodide that a positively charged o-tolyl ion was involved and that a radical mechanism could be excluded.

On the ground of the I-I distance in diphenyliodonium iodide, determined by means of X-ray investigation, Medlin (11) had already come to the conclusion that the I-I bond was ionic and not covalent.

However, an ionic bond in the iodonium iodide did not fully exclude the formation of radicals as a result of breaking a covalent bond in the thermal decomposition of iodonium salts. Sandin and co-workers (5) pointed out the significant fact that the decomposition temperature of certain iodonium salts decreased with increasing nucleophilicity of the anion. The decomposition temperatures for the bromide, iodide, and sulphide of di-o-tolyliodonium are respectively 178°, 155° and room temperature. For a truly ionic compound without the least covalent character in the iodonium iodine - anion bond the temperature at which decomposition occurs would be expected to be independent, or almost so, of the nature of the anion. These workers found that diphenyliodonium chloride and di-p-tolyliodonium chloride in boiling n-propyl alcohol arylated mercury and tellurium, and that diphenyliodonium sulphide arylated antimony or tellurium at room temperature. They concluded that the iodine atom in the iodonium salt was able to expand its valence shell to a decet,

giving an unstable tricovalent iodine compound that produced radicals when it decomposed:



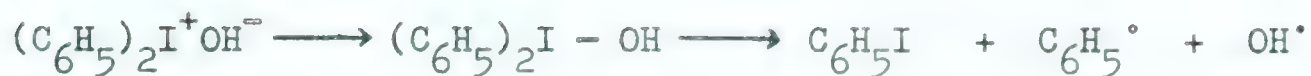
This behaviour was analogous to that of decomposing benzenediazonium chloride in acetone, which was found to arylate mercury, tellurium, and antimony under similar conditions (12).

Masson and Race (13) had already suggested earlier that a covalent intermediate played an important role in the irreversible fissions that iodonium compounds undergo and they had isolated 4,4'-dichlorodiphenyliodonium hydrogensulphate in an oily form, partly soluble in chloroform.

The work described so far has been reviewed already by Sandin (14).

Work on the reactions between diphenyliodonium salts and compounds containing a thiol group (thioglycolic acid, thiophenol, cysteine) by Sandin and co-workers (6) showed that yellow precipitates or yellow solutions were produced, the colour of which disappeared rapidly. As before (5) tellurium was phenylated under the appropriate experimental conditions by the reaction mixtures containing the unstable yellow products.

When pyridine was added to a boiling aqueous solution of diphenyliodonium chloride no appreciable decomposition of the salt seemed to occur. After adding sodium hydroxide to this solution there was an immediate vigorous reaction and a mixture of 2-, 3-, and 4-phenylpyridines could be isolated in addition to a large quantity of iodobenzene. No phenol or chlorobenzene could be detected. These results led Sandin and Brown (15) to believe that probably diphenyliodonium hydroxide was the active intermediate and they formulated its decomposition via a tricovalent iodine compound:

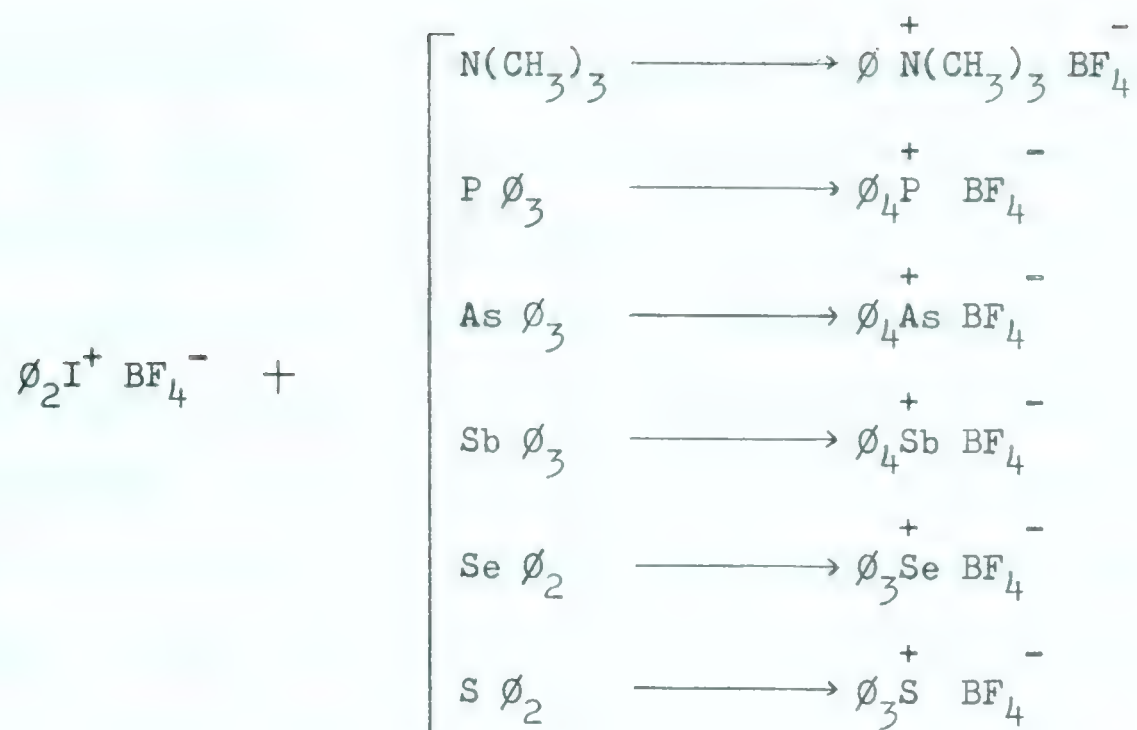


Iodonium hydroxides are thought to exist in solution only. They are strong bases, analogous to quaternary ammonium bases and tertiary sulphonium bases. No pure solid iodonium hydroxides have been isolated and described in the literature (16, 17). Mascarelli and Gatti (18) treated a suspension of dibenziodolium iodide in water with silver oxide. From the strongly alkaline solution they isolated a yellowish precipitate. The analysis indicated that it was a mixture of dibenziodolium hydroxide and its bicarbonate. The only explanation for the presence of bicarbonate would be that the solution absorbed carbon dioxide from the air.

In the present work the preparation of a solid crystalline iodonium hydroxide is described.

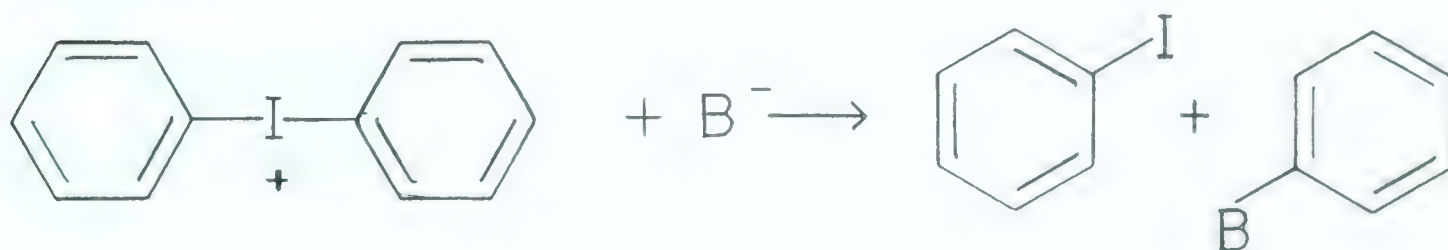
Contrasting with the previously mentioned homolytical phenylation of mercury, selenium, tellurium, and pyridine, as carried out by Sandin and co-workers (5, 6, 15) with the aid of diphenyliodonium compounds, is the preparation of many onium fluoborates by phenylation with diphenyliodonium fluoborates, as carried out by Nesmeyanov and collaborators (19, 20). The equations of some of these reactions are given on the next page. The yields were in general excellent. Heterolytic cleavage of the iodonium salt occurs here when the anion has no or very little nucleophilic properties.

Under the same reaction conditions $(\text{C}_6\text{H}_5)_3\text{Sb}$, $(\text{C}_6\text{H}_5)_3\text{As}$, $(\text{C}_6\text{H}_5)_2\text{Se}$, and $(\text{C}_6\text{H}_5)_2\text{S}$ were not phenylated by diphenyliodonium chloride.



C_6H_5 = phenyl

In 1953 Beringer and co-workers began their series of papers on the synthesis, properties, and reactions of diaryliodonium salts. They found that a wide variety of organic and inorganic bases were phenylated when they were heated in an aqueous or alcoholic solution of diphenyliodonium bromide or its 2-, and 3-nitroderivatives (21):

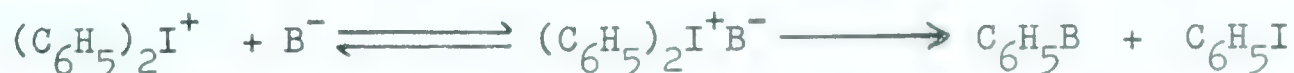


There were strong indications that nucleophilic rather than a radical attack took place on the 1-carbon atoms of the diphenyliodonium salt. When 2-, or 3-nitrodiphenyliodonium bromide was used, attack of

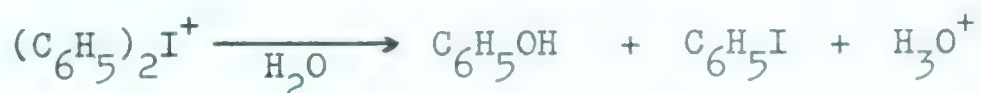
the bases occurred at the 1-carbon atom of the substituted phenyl ring. The rates of reaction and the yields increased in the order unsubstituted < 3-NO₂- < 2-NO₂-diphenyliodonium bromide and the increased reactivity of the nitro compounds was explained "on the basis that there would be more interaction of an electron withdrawing group with a ring electron-rich in the transition state during nucleophilic attack than with a ring neutral in the ground state". In these first experiments of Beringer's group benzene was never detected as a by-product; its formation would have indicated a mechanism involving radicals.

In their subsequent papers Beringer and co-workers reported the study of the kinetics of the reaction of diphenyliodonium cation and phenoxide ion (22), halide ion and hydroxylic solvents (23, 24).

The decomposition of diphenyliodonium bromide in a refluxing dilute aqueous solution to bromobenzene and iodobenzene was extremely slow, faster in diethylene glycol and still faster in dimethylformamide. Beringer thought that these and several other reactions of the diphenyliodonium ion which were studied proceeded through ion pairs whose concentration and rate of decomposition increased as the dielectric constant and solvating power of the medium decreased (16). The ion pairs were thought to decompose irreversibly by the way of an activated complex or transition state, the concentration of which determined the reaction rate:



During the decomposition of diphenyliodonium bromide in water hydrolysis was a competitive reaction:

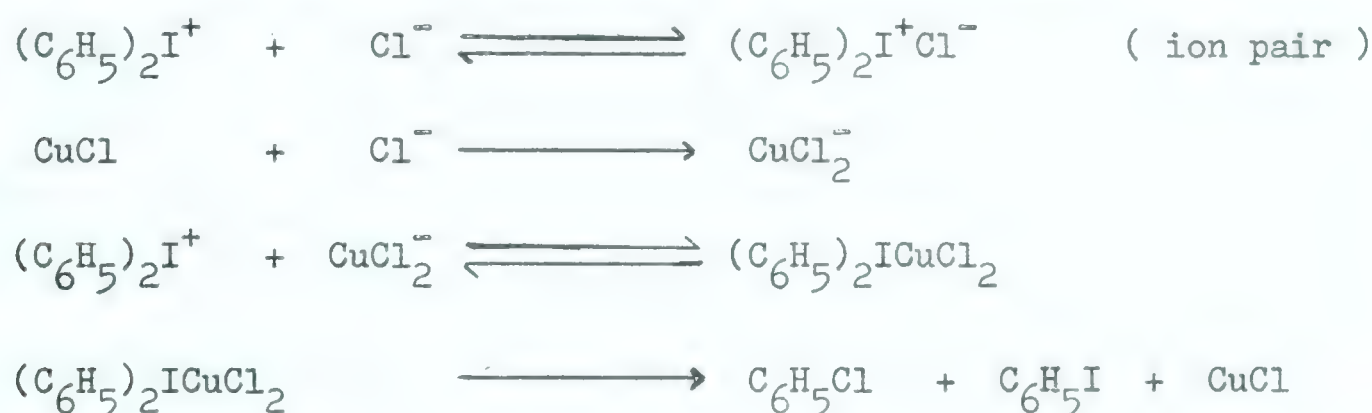


About 10% of the iodonium salt decomposed into phenol and iodobenzene.

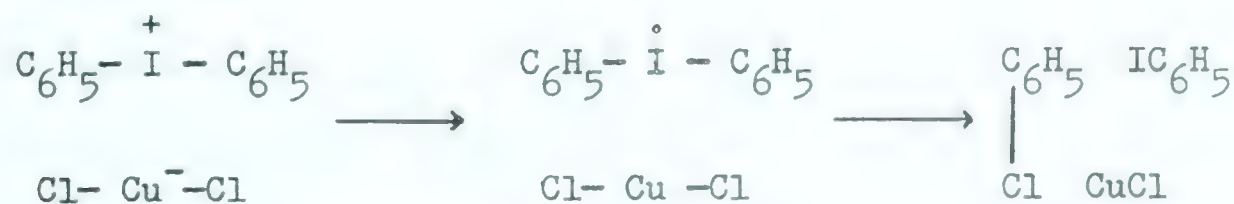
Büchner who studied the decomposition of diphenyliodonium chloride in aqueous solution at 99.1° had found in 1903 that the rate of decomposition was strongly influenced by the presence of traces of iodine, free base (the hydroxide), or acid (25).

Beringer (22, 23) found that the second phase (iodobenzene and bromobenzene) that was formed in the experiments that were carried out in water had an accelerating effect on the decomposition, and that copper salts catalyzed the reaction very strongly.

Later it was found that cuprous ion was the catalyst proper and the following tentative mechanism was proposed for the catalyzed decomposition of diphenyliodonium chloride in diethylene glycol (23) :

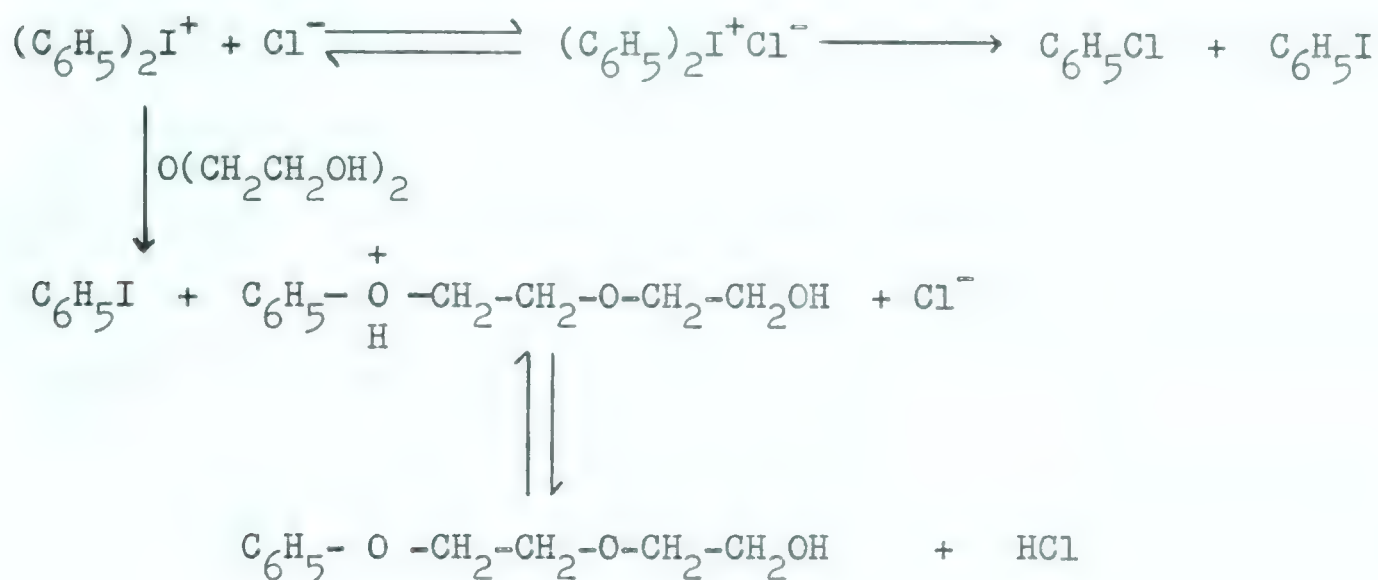


The nature of the diphenyliodonium-cuprochloride complex could not be defined but it was found later that diphenyliodine $(\text{C}_6\text{H}_5)_2\text{I}^\bullet$ was apparently formed (26) in the electroreduction of diphenyliodonium cation, which decomposed instantaneously with formation of iodobenzene and biphenyl. The complex was considered to be an ion pair, which decomposed as follows:



The data obtained from the study of the hydrolysis of diphenyliodonium salts were so unreliable that no rigorous kinetic analysis of

the results was possible (23). After having studied the decomposition of diphenyliodonium chloride in diethylene glycol Beringer (23) proposed the following tentative mechanism:



The quantity of hydrochloric acid formed was small but it catalyzed the decomposition into chlorobenzene and iodobenzene. Addition of potassium chloride, a common salt, which was expected to decrease the concentration of free diphenyliodonium ion, indeed decreased the amount of acid formed. Addition of an inert salt, in this case potassium p-toluenesulphonate, caused a strong increase of the solvolysis by enhancing the ionizing power of the solvent.

After these experiments the authors (23) concluded: "It seems that the reaction of the diphenyliodonium cation with one of the water or glycol molecules of its solvent cage is inhibited by a paired chloride ion which is probably located close to the iodine atom!"

Except for the decompositions that were found to be catalyzed by cuprous ion Beringer and coauthors had not suggested a radical mechanism for the decomposition of diphenyliodonium salts until in their last publication on this subject (24) they proposed a covalent diphenyliodonium hydroxide as an intermediate in the decomposition of the tosylate in dioxane - water containing alkali:



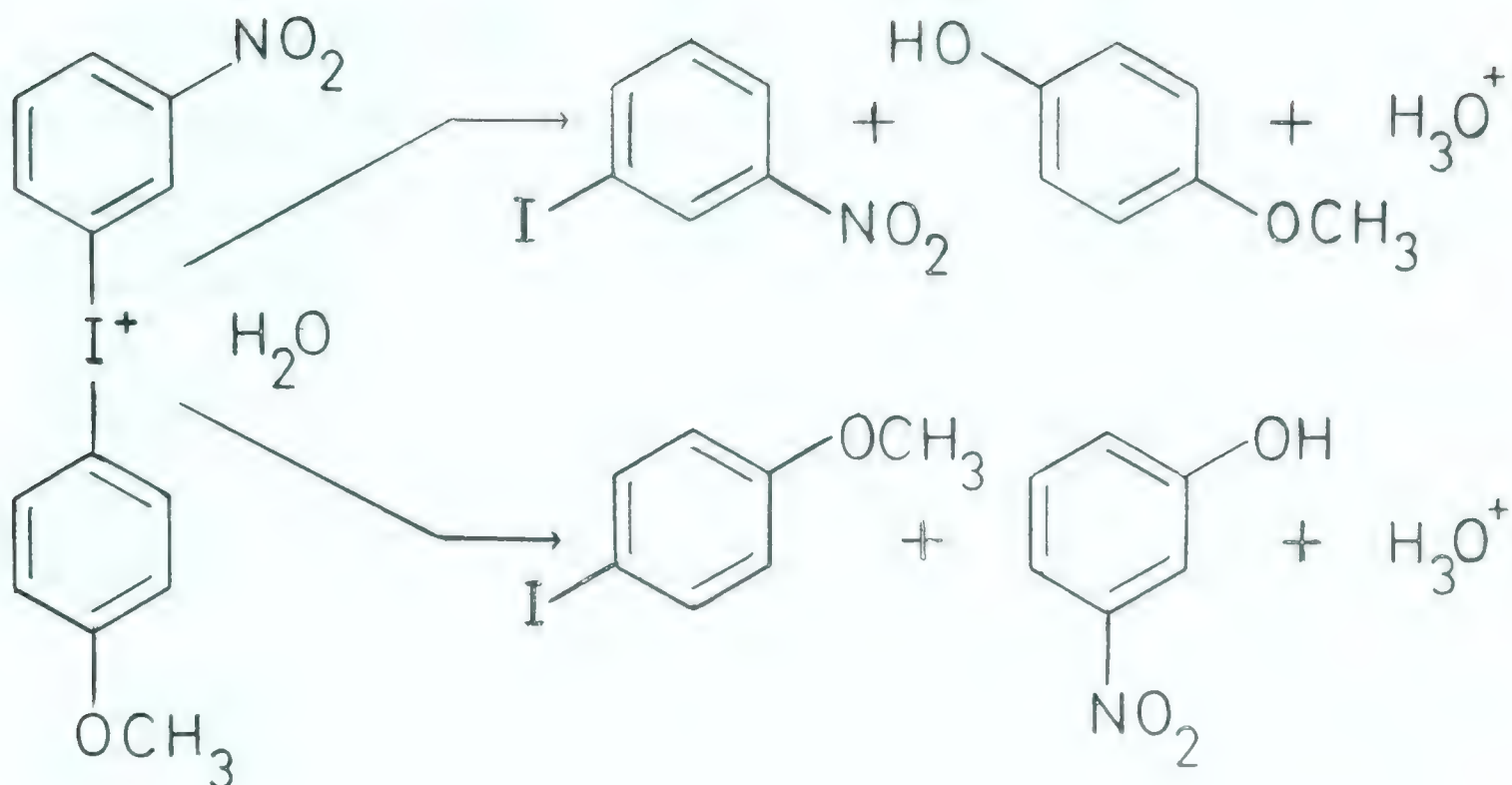
Sandin and Brown had suggested this covalent hydroxide earlier (15). In the mean time benzene had also been isolated after hydrolysis of diphenyliodonium chloride in an alkaline dioxane - water mixture (24).

Beringer and his co-workers in their study of the kinetics of the hydrolysis and related reactions of diphenyliodonium salts had used many experimental variations and their results became more and more puzzling and difficult to interpret.

Caserio, Glusker, and Roberts (17) in 1959 published definite evidence for a radical mechanism operating in the hydrolysis of some substituted diphenyliodonium salts. They reasoned that to study the hydrolysis the anions should have little or no nucleophilic character, because the chloride ion still interfered with the hydrolysis reaction so strongly that it hardly took place at all (as had been found to be the case in Beringer's studies).

The anions selected for the investigation were fluoride, fluoborate, tosylate, and trifluoroacetate. Unsymmetrically substituted diphenyliodonium cations were used, one of which, 3-nitro-4-methoxydiphenyliodonium, was selected because its substituents had extreme and opposite polar character.

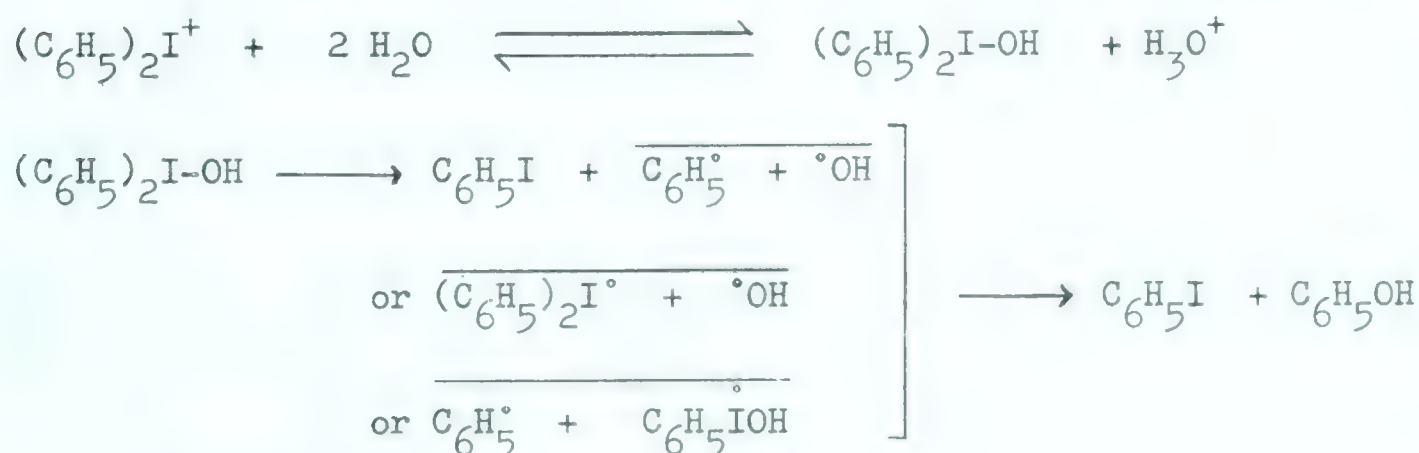
It was found that the direction of bond fission in the hydrolysis of unsymmetrical iodonium salts was little influenced by the polar nature of the substituents present and that the product distribution remained unchanged on varying the anion associated with a given iodonium cation.



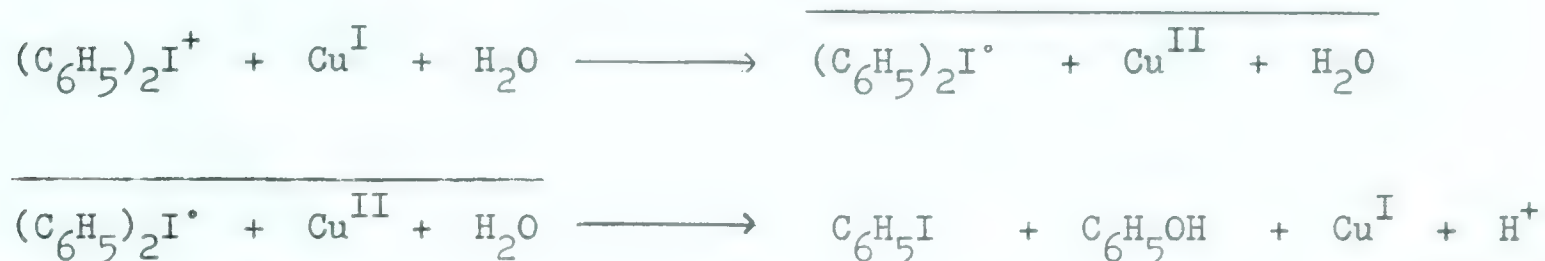
Most hydrolyses were carried out in water but aqueous dioxane or acetonitrile were used too. The hydrolysis in aqueous dioxane was catalyzed as a result of oxygen- or peroxide-induced decomposition of dioxane. However, the product distribution was not significantly influenced by changes in the solvent or by the presence of cuprous or cupric salts, which catalyzed the hydrolysis. Cuprous copper was found to be the catalyst proper.

The uncatalyzed reaction in water was retarded by acid formed during the hydrolysis and by acid when added initially.

All these results very strongly indicated a radical mechanism and the authors offered this mechanism for the uncatalyzed hydrolysis:

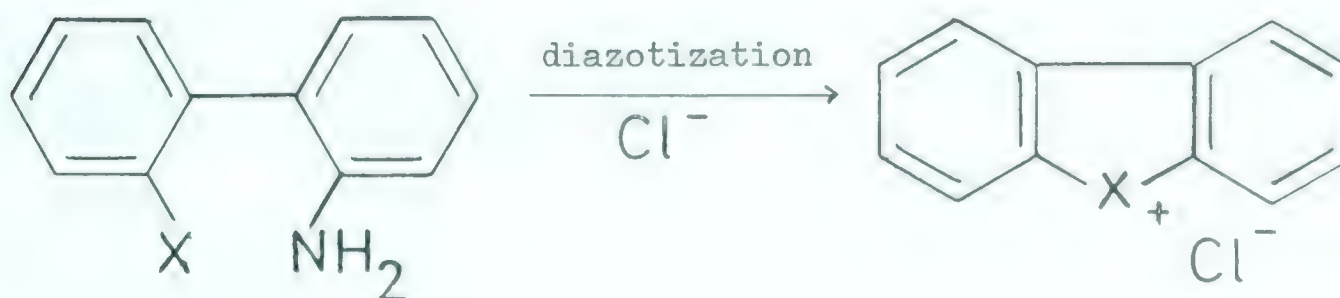


The superscript bars indicate solvent-caged radical pairs. The species $(\text{C}_6\text{H}_5)_2\text{I}^\bullet\text{-OH}$ might decompose in more than one way, Roberts and co-workers thought. For the hydrolysis catalyzed by cuprous ion they proposed the following mechanism (17, 27):



Because acid had no apparent effect on the rate in the presence of cuprous copper the step in which diarylhydroxyiodine is formed was not admissable in a reaction scheme in the presence of this catalyst. The diaryliodine was not visualized to be a "free" radical but instead held in a solvent cage with water-solvated cupric copper. These radicals were thought to be short-lived, reacting with each other in pairs as they were produced, and without dimerization or hydrogen abstraction. Products that were expected to be formed by such processes were never isolated by Roberts and his collaborators. It has been mentioned already that Beringer (24) isolated benzene after hydrolysis of diphenyliodonium chloride in alkaline dioxane - water.

So far only iodonium compounds have been dealt with. In 1952 Sandin and Hay (28) prepared the first bromonium and chloronium compounds by diazotization of 2-halogeno-2'-aminobiphenyls. Dibenzobromolium and dibenzochlorolium salts were obtained:



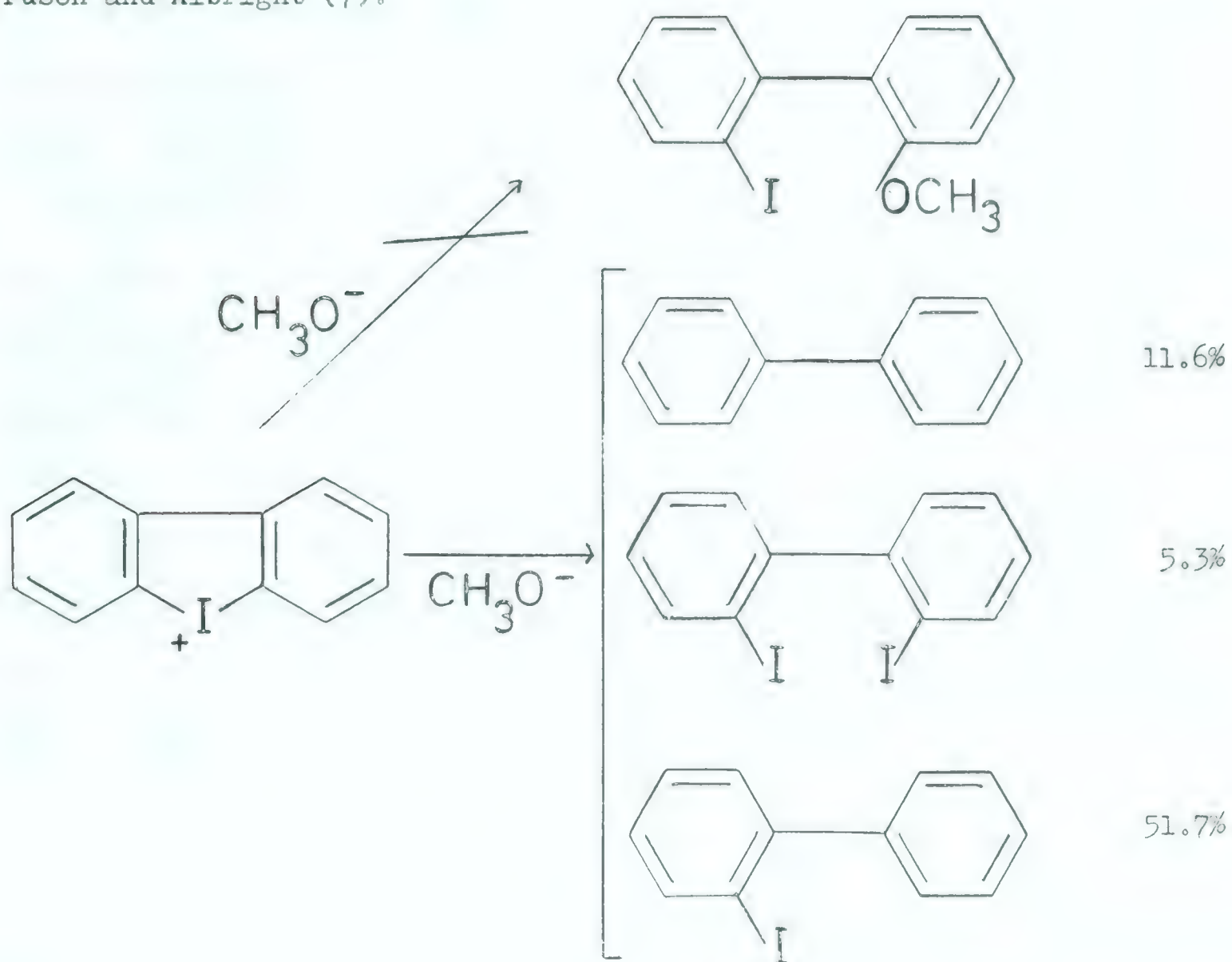
A few years later Nesmeyanov and co-workers reported the preparation of substituted diphenylbromonium (29) and diphenylchloronium (30) salts by heterolysis of the appropriate aryldiazonium fluoborates in bromobenzene and chlorobenzene respectively. The yields of this reaction are very low, the highest obtained being 6% of the theoretical. It is interesting that diphenyliodonium salts can not be prepared by this method from iodobenzene. These bromonium and chloronium salts are excellent arylating agents.

Diphenylbromonium and diphenylchloronium fluoborates do not react with metallic mercury but the iodides do in an alcoholic medium. If a homolytic reaction is assumed to occur this means that the electron octet of the bromine and chlorine atoms is extended to a decet giving a covalent halonium iodide (19).

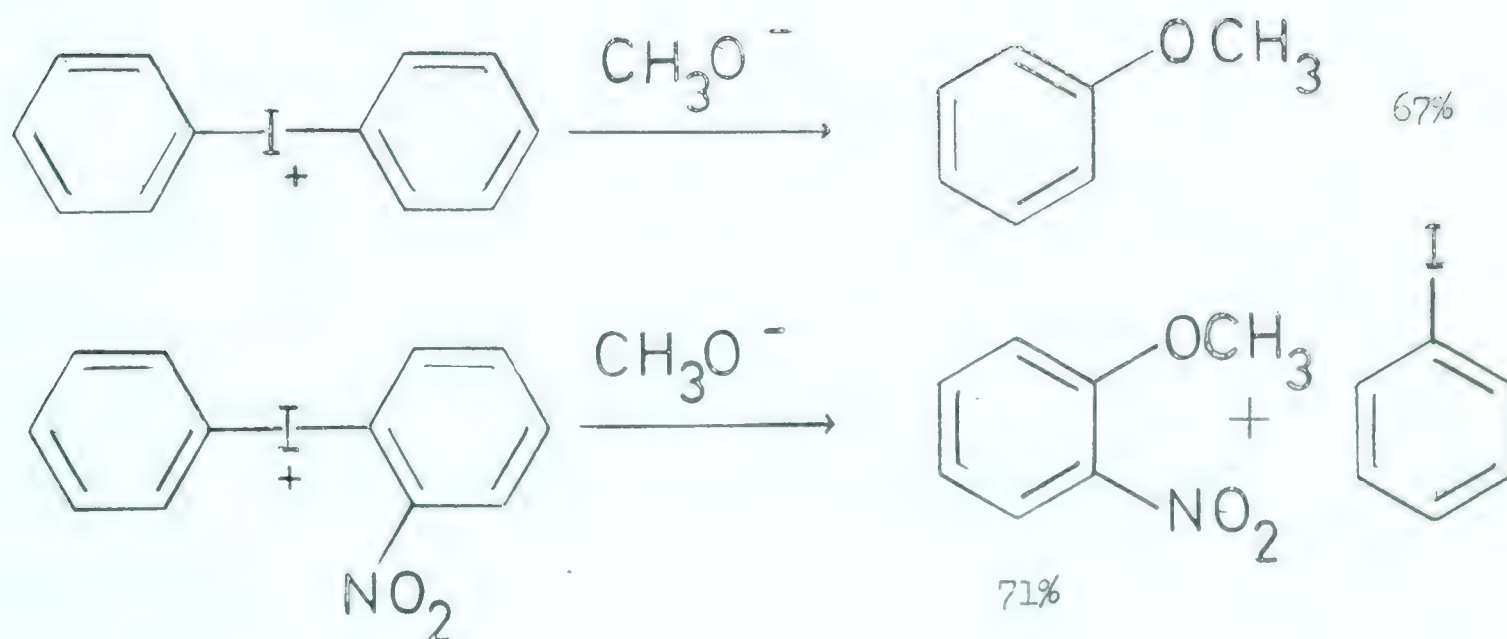
In an attempt to prepare 2-iodo-2'-methoxybiphenyl Fuson and Albright (7) treated dibenziodolium sulphate with sodium methoxide in refluxing methanol. The desired compound could not be isolated and the authors concluded that nucleophilic displacement with methoxide ion in the cyclic iodonium salt was apparently much more difficult to accomplish than in the "open" diaryliodonium compounds.

Instead they isolated biphenyl, 2-iodobiphenyl, and 2,2'-diiodobiphenyl; 20% of the dibenziodolium compound was recovered as the chloride. Fuson and Albright did not interpret this result but it certainly strongly indicates a radical mechanism and a different behaviour of the cyclic iodonium compound compared with that of diphenyliodonium bromide under the same reaction conditions. Beringer and co-workers (21) have shown that anisole is formed in good yield.

Fuson and Albright (7):

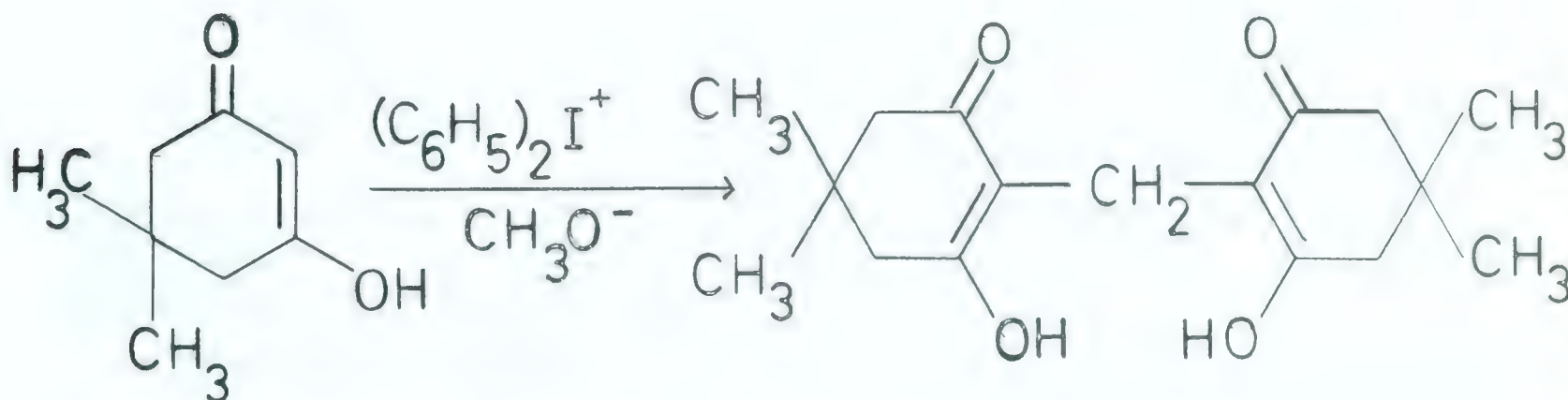


Beringer and co-workers (21):



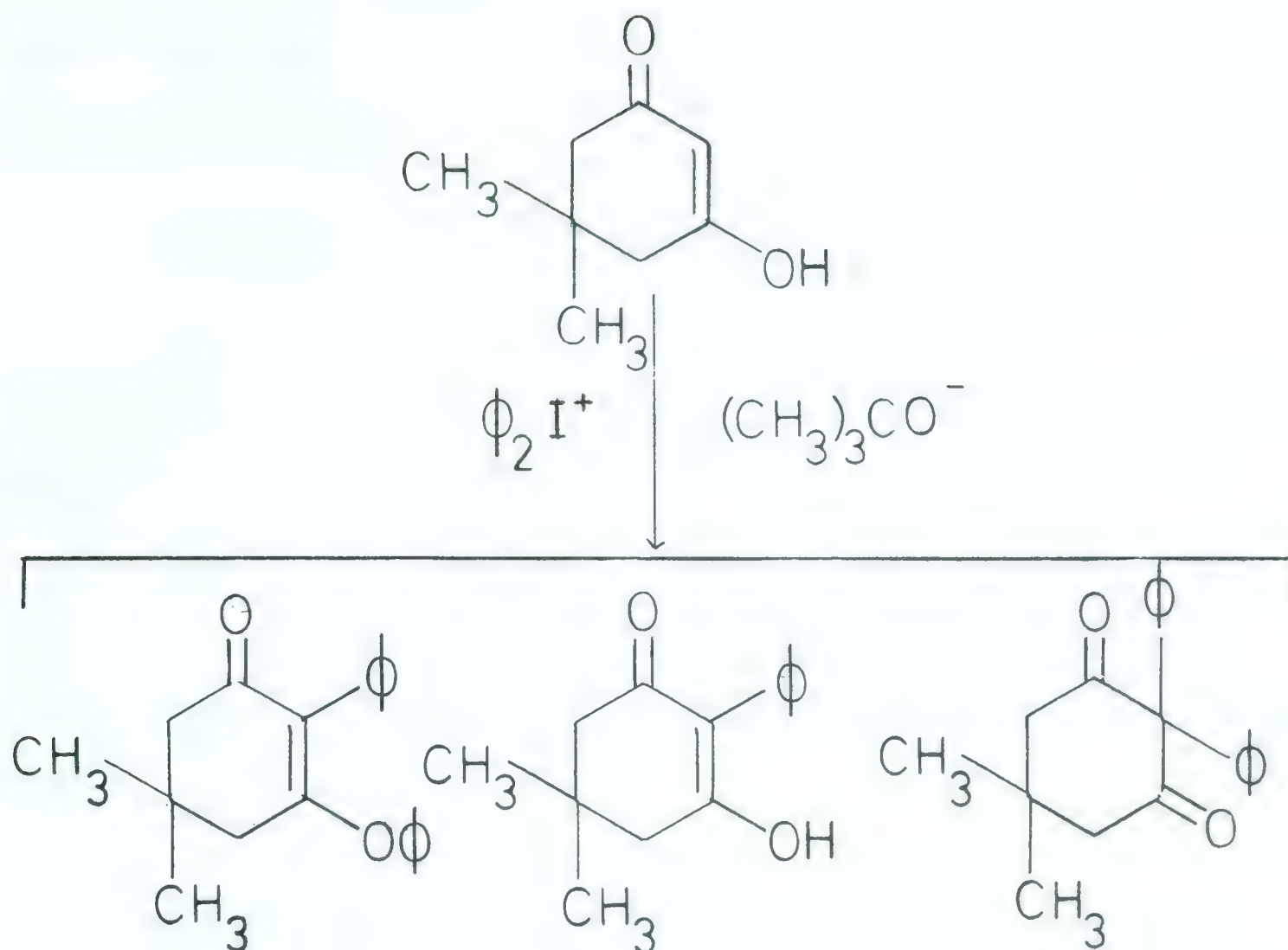
About a year after Fuson and Albright's paper (7) Beringer and co-workers published the results they had obtained in the phenylation of dimedone with diphenyliodonium salts (8). In the following description of their work and throughout the rest of this thesis the present author will often use the trivial name dimedone instead of the systematic names 5,5-dimethyl-1,3-cyclohexanedione or 5,5-dimethyl-1-cyclohexenol-3-one but with their numbering system. Phenyl ethers of the enolic forms of the ketones are named as O-phenyl derivatives.

When Beringer tried to arylate dimedone with diphenyliodonium chloride or bromide and sodium methoxide or ethoxide in the corresponding alcohols, the desired products were not obtained but the dimedone derivatives of formaldehyde and acetaldehyde were isolated.



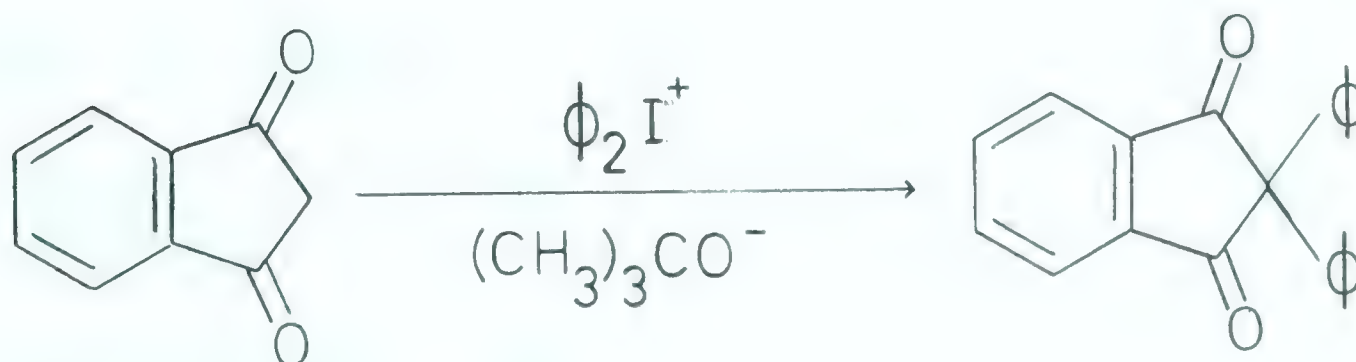
The alcohol was apparently dehydrogenated in the presence of dimedone. The authors did not try to explain this result, but in a more recent publication (31) they implied that a radical mechanism is responsible for this dehydrogenation.

When t-butyl alcohol and sodium t-butoxide were used instead of the primary alcohols and their alkoxides, 2-phenyldimedone and 2,2-diphenyldimedone were formed in modest yield and O,2-diphenyldimedone was isolated in low yield and only when the reaction was carried out at low temperatures.



Dimedone could also be phenylated in aqueous solution with diphenyliodonium chloride in the presence of sodium hydroxide at reflux temperature. Only 2,2-diphenyldimedone was isolated.

Very recently Beringer, Galton, and Huang (32) reported the phenylation of 1,3-indandione with diphenyliodonium chloride in t-butyl alcohol:



In the presence of isopropyl alcohol, acetone was formed. The influence of radical scavengers, oxygen or styrene, on the yield of phenyl-

ated product and the formation of benzene and biphenyl clearly indicated a radical mechanism. The authors proposed as a first step the reversible formation of a radical pair



without suggesting a covalent iodonium compound as an intermediate, as Beringer had done earlier (24).

The phenylation of dimedone in aqueous solution was independently carried out by Russian workers (33), who obtained all three products mentioned before and in addition isolated a very small quantity of O-phenyl-dimedone.

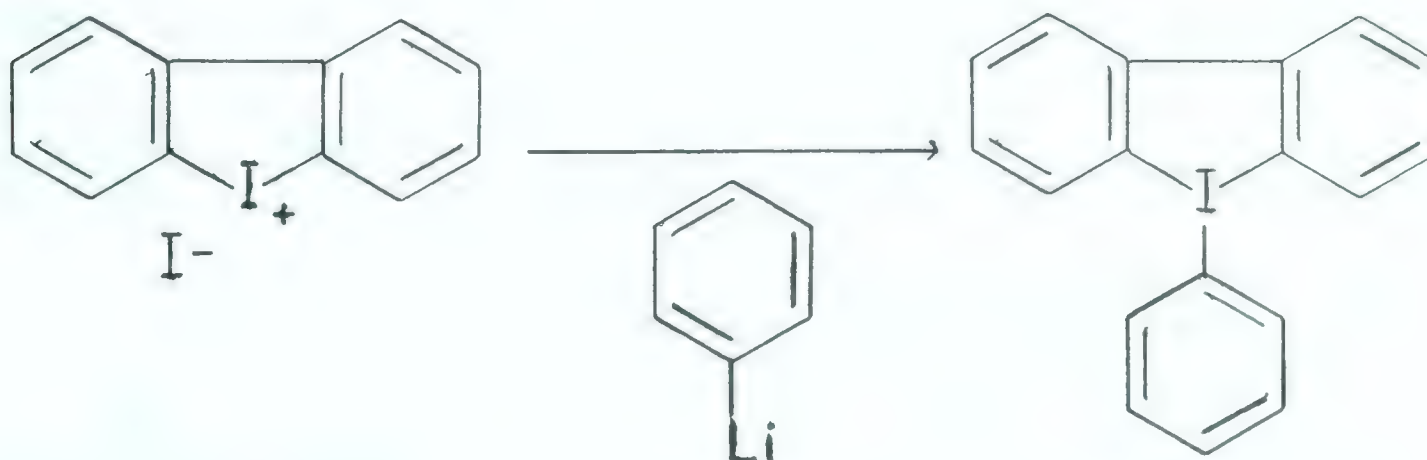
In the preceding pages unstable compounds containing tricovalent iodine have been mentioned several times as precursors to radical species. The first triaryliodine, triphenyliodine, was described in 1949 by Wittig and Rieber (1). It was prepared from diphenyliodonium iodide, suspended in ether, to which was added a solution of phenyllithium. When the reaction was carried out at -80° they obtained yellow crystals which decomposed at -10° to biphenyl and iodobenzene.

Another method of preparation was used later by Wittig and Clauss (2) when they used phenyliodoso dichloride as their starting material:



Thirty years earlier Hepworth (34) had treated phenyliodoso dichloride with phenylmagnesium bromide at room temperature, after which he isolated biphenyl, iodobenzene and a very small quantity of diphenyliodonium salt.

All reactions involving triphenyliodine were carried out by Wittig in a nitrogen atmosphere. When the compound was slowly warmed to 20° it exploded with great force. In 1955 Clauss (3) described the preparation of 5-phenyldibenziodole using the method of Wittig and Rieber (1). This yellow compound was much more stable than triphenyliodine and could even be recrystallized from tetrahydrofuran. It decomposed at 105° but in a nitrogen atmosphere it could be kept for a few days at room temperature without decomposition. With hydrogen chloride in absolute ether or with triphenylboron in benzene dibenziodolium salt was formed again.

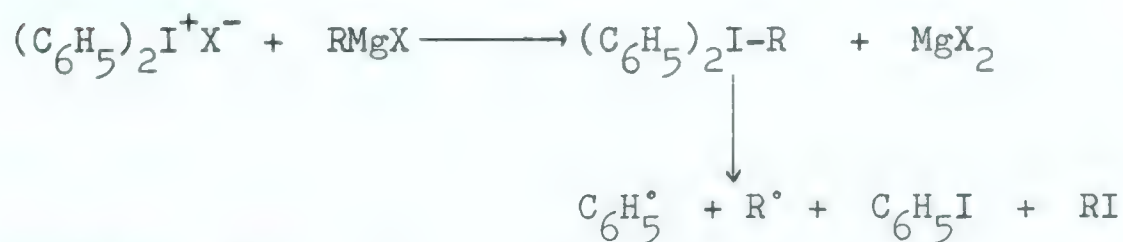


The present author has also prepared 5-phenyldibenziodole and found that it could be stored for more than a week in a nitrogen atmosphere at 4°; all attempts to recrystallize the compound from tetrahydrofuran or other solvents resulted in rapid decomposition, however.

In one of their first publications on diaryliodonium salts Beringer and co-workers (21) described the reaction between diphenyliodonium bromide and methyl-, ethyl-, and phenylmagnesium bromide (or phenyllithium) at room temperature. After completion of the exothermic reaction toluene, ethylbenzene, and biphenyl could be isolated, respectively. The authors did not explain these results in the light of Wittig and Rieber's work (1) although they referred to their paper, but thought

that these products were formed as a result of nucleophilic attack of the organometallic compound on the 1-carbon atom of the diphenyliodonium ion.

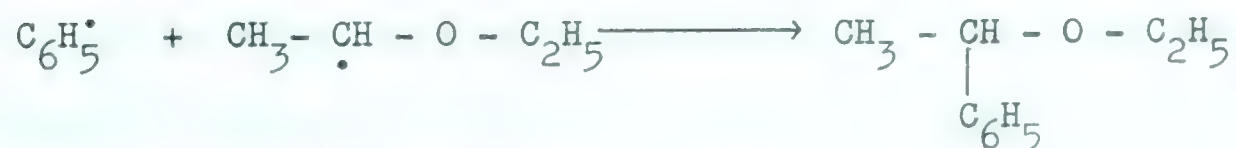
More recently Beringer (31) repeated these reactions under various conditions. When the iodonium salt was added to the ethereal solution of Grignard reagent at reflux temperature a yellow colour was visible, disappearing immediately. Below 0° a yellow-orange precipitate was formed that rapidly decomposed at higher temperature. The formation of products isolated in many runs with various Grignard reagents could be explained in terms of a radical decomposition of the intermediate trisubstituted iodine:



R= Alkyl

The following compounds were isolated: biphenyl, alkylbenzenes, iodo-benzene, alkyl iodides, and benzene.

The benzene may have been formed by hydrogen abstraction from the solvent diethyl ether because the ethyl ether of methylphenylcarbinol was sometimes isolated as well:



The mechanism of this reaction has not been proven, but it is clear that radicals must play an important role.

The present author was interested in the possibility of preparing trisubstituted bromine or maybe even chlorine compounds. These were expected to be very unstable and, in fact, none were isolated.

Both trisubstituted iodines that have been described in the literature (2, 3) have a bright yellow colour. The yellow colour of certain iodonium compounds has been noted several times. These compounds were often unstable and in their decomposition the formation of radicals was many times indicated.

In 1894 Hartmann and Meyer treated a solution of diphenyliodonium hydroxide with sodium sulphide and obtained the yellow sulphide, which decomposed immediately into iodobenzene and diphenylsulphide (4). The same sulphide was later prepared by others (5). In 1947 Sandin and co-workers (6) found that diphenyliodonium chloride reacting with thiolate anion in general produced either a transient yellow colour or a yellow precipitate.

Lewis and Stout (35) observed that a yellow colour was produced when diphenyliodonium cation reacted with hydroxide or phenoxide anion. When they mixed solutions of diphenyliodonium chloride, phenol, and sodium hydroxide at room temperature a yellow oil was sometimes formed, which was soluble in sodium hydroxide solution with a yellow colour, but gave a colourless solution in acid. These reactions were reversible but did not consume the iodonium ion.

Beringer and Gindler (22) observed a yellow colour immediately after mixing diphenyliodonium and phenoxide solutions in water - dioxane. The colour disappeared on acidification. This led them to believe that, maybe the interaction between the ions was not purely coulombic, but they interpreted their results in terms of ion pairs.

The present author has been able to prepare a stable yellow compound from dibenziodolium cation and 2-naphthalenethiolate anion. In addition several dibenziodolium salts have been prepared that form colourless crystalline hydrates but yellow anhydrous compounds. This change was found to be reversible and could be effected very smoothly.

SECTION 2

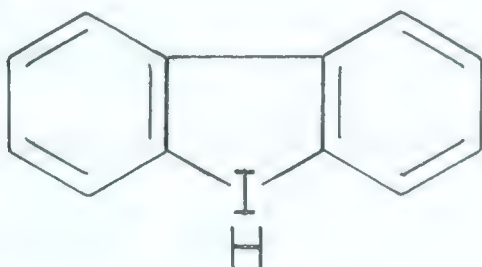
R E S U L T S A N D D I S C U S S I O N S

P a r t I

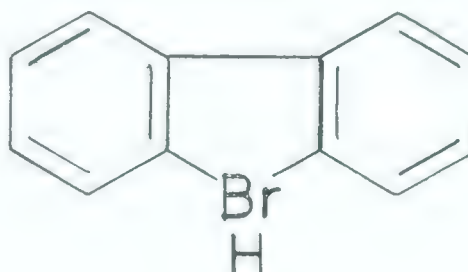
Attempts to Prepare Derivatives of the Unknown

Compound Iodole and its Bromine Analogue

When work was started on the preparation of some dibenziodoles that were substituted on the iodine atom this was mainly done to gain experience in handling these unstable compounds and to find the best method. The final goal was the preparation of a derivative of dibenzobromole.



Dibenziodole (unknown)

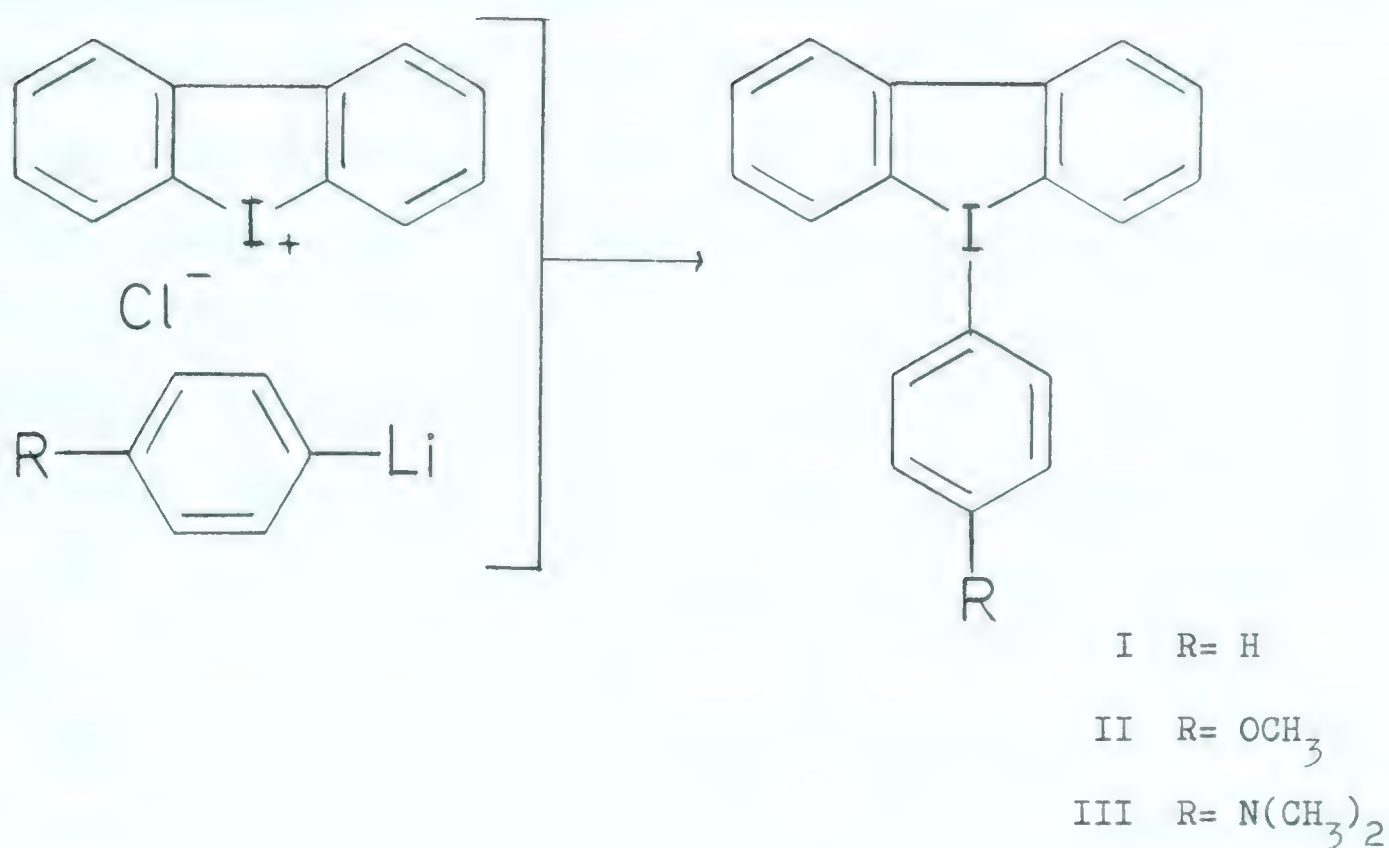


Dibenzobromole (unknown)

As the reaction itself and, more in particular, all subsequent manipulations would have to be carried out in a nitrogen atmosphere, a dry-box filled with nitrogen was used.

The first compound that was prepared, 5-phenyldibenziodole (I), was known already (3).

Solutions of phenyllithium were prepared from bromobenzene or diphenylmercury and lithium. The results in the final reaction were the same with each of these solutions.



When the ethereal solution of phenyllithium was added to the suspension of dibenziodolium salt in ether there was always a slight heat effect and the mixture became yellow. The brightly yellow solid product that was isolated decomposed between 95 and 115°. Clauss reported for the recrystallized material decomposition between 105 and 115° (3).

The present author found it impossible to recrystallize this material from tetrahydrofuran (peroxide-free) because rapid decomposition occurred. All other solvents that were tried were found to be unsuitable. In ethanol and methanol the solubility was too low, in chloroform, carbontetrachloride, benzene, and toluene the product decomposed rapidly. When 5-phenyldibenziodole was stored at 3-4° under nitrogen it decomposed only slowly.

The reaction between dibenziodolium chloride and p-methoxyphenyllithium or p-dimethylaminophenyllithium yielded brightly yellow products which probably had the structures II and III. They seemed to decompose more readily than 5-phenyldibenziodole and decomposition became

especially rapid when a vial wherein the compound was stored under nitrogen had been opened for a few seconds, letting in some air.

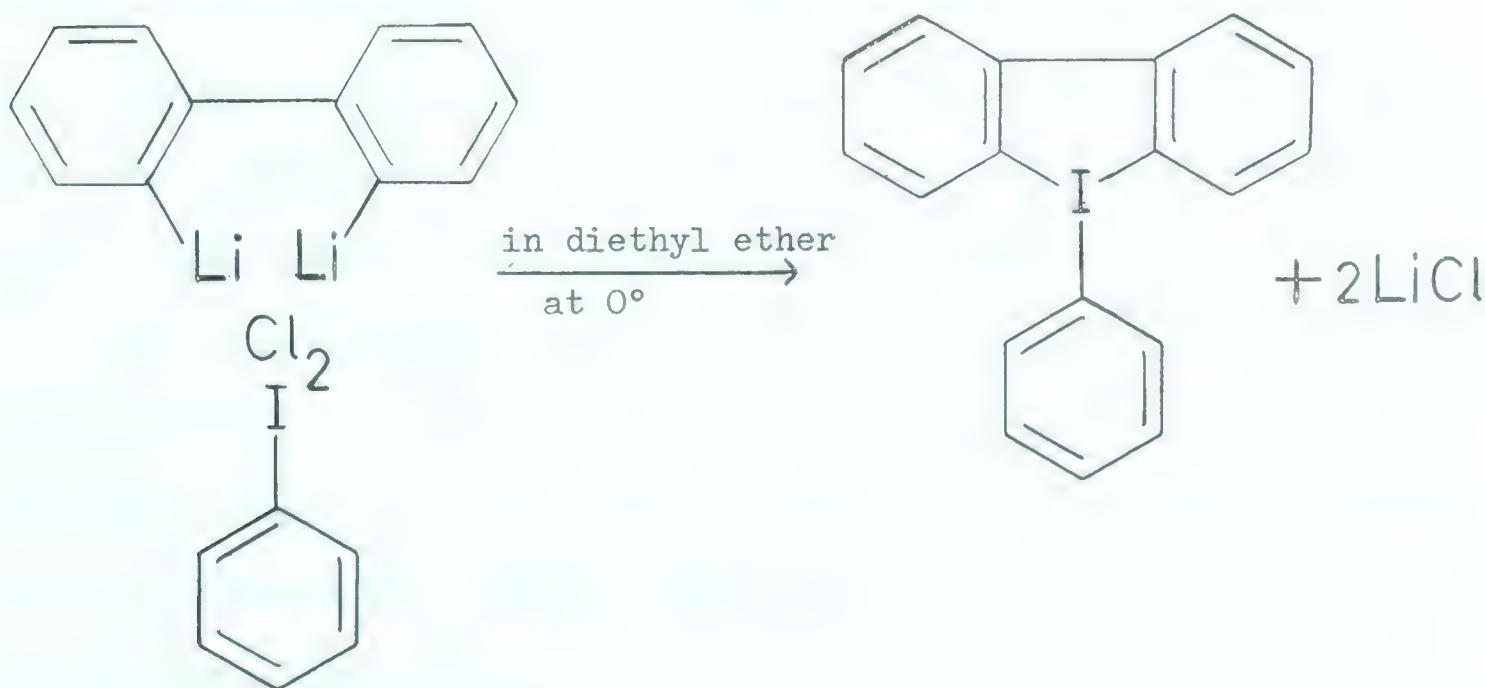
The infrared spectrum of 5-phenyldibenziodole showed the numerous absorption peaks of the dibenziodolium system, most of which are weak. In addition there were absorption bands at 696 and 730 cm^{-1} , the first of which is a strong indication for the presence of the monosubstituted phenyl group. However, these absorptions may also be caused by iodobenzene which is one of the possible decomposition products of 5-phenyldibenziodole.

The fact that decomposition occurred rapidly in the solvents that were used made the ultraviolet spectra that were taken useless. The present author feels that unfortunately both the infrared and the ultraviolet spectra can not be used as a basis for discussion.

Wittig and Clauss (2) found a second method for the preparation of triphenyliodine, using phenyliodoso dichloride as starting material:

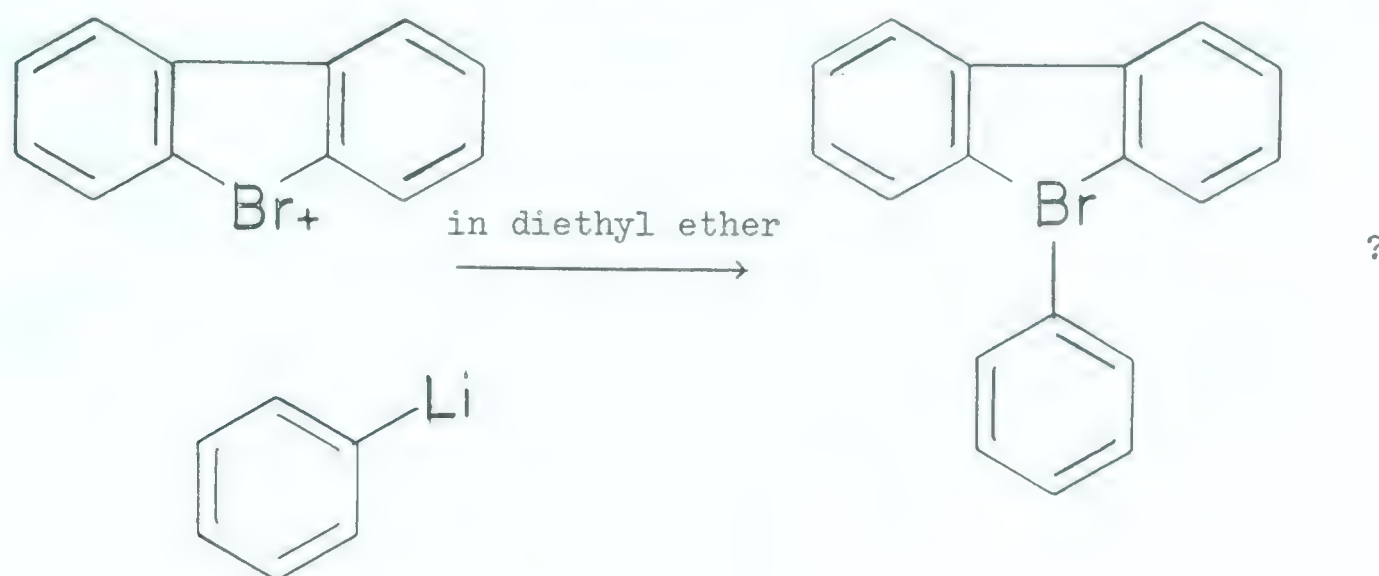


In the present work an attempt was made to prepare 5-phenyldibenziodole in a similar way:



The desired compound could not be prepared in this manner ,
however.

Because it was expected that the product of the reaction between dibenzobromolium chloride and phenyllithium would be very unstable the reaction was carried out under nitrogen at temperatures between -75 and -15° in a series of small-scale experiments:

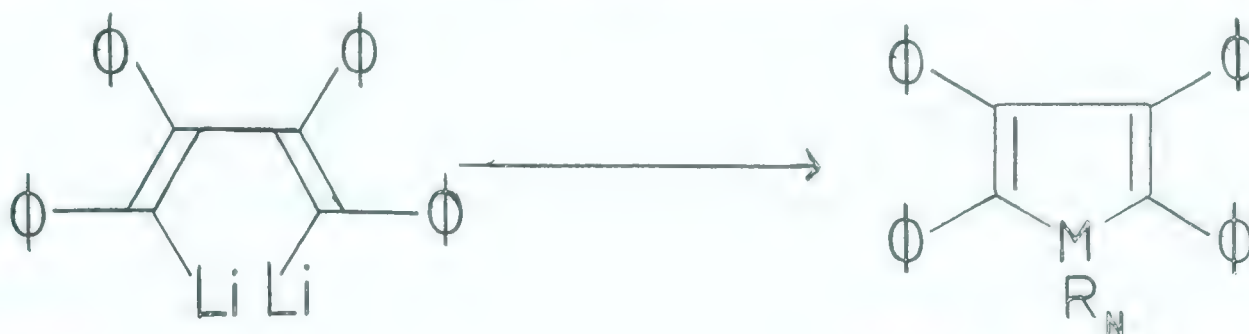


It was hoped that by choosing a low enough temperature it would be possible to prevent immediate decomposition. At room temperature and down to -30° the reaction between phenyllithium and the dibenzobromolium salt was instantaneous and vigorous without the visible formation of a solid reaction product. At -45° the reaction seemed to be much slower and a rapidly fading yellow colour could be observed.

The final experiment was carried out on a larger scale. A solution of phenyllithium, cooled to -80° , was added to a suspension of dibenzobromolium chloride in ether which was kept at -60° . The reaction mixture turned yellow but this colour faded in ten minutes and a grey solid was formed. When a small quantity of this material, which had been kept at -75° , was removed from the reaction flask on a spatula it decomposed with

a small dull explosion when its temperature rose. It was clear that, whatever the nature of the product, it was very unstable. The investigation of this reaction was not continued any further.

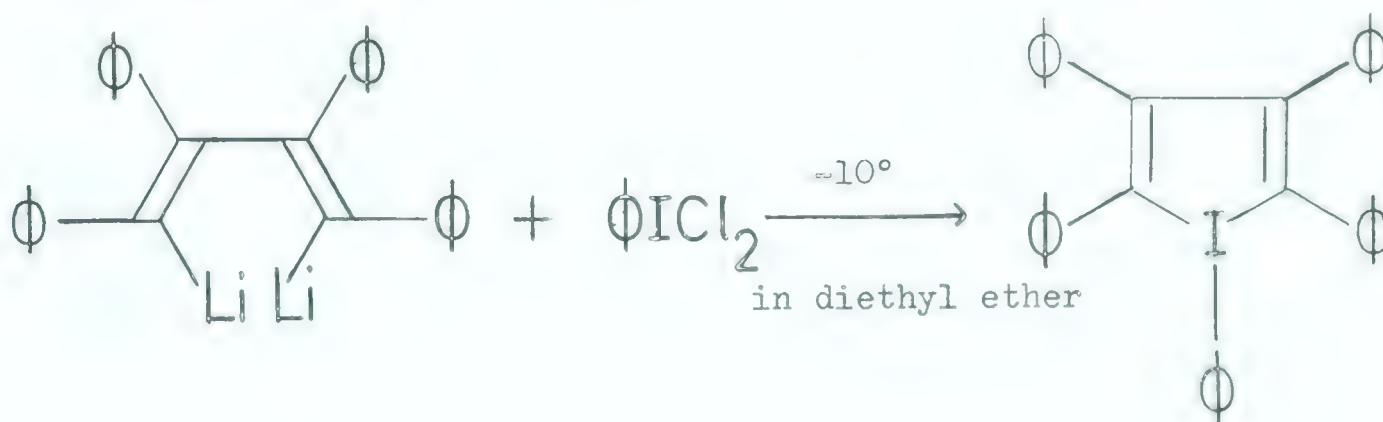
Between 1959 and 1961 Braye and co-workers (36, 37) and Leavitt and co-workers (38, 39) published the results they had obtained in the synthesis of some substituted unusual heterocyclopentadienes. Both groups used 1,4-dilithio-1,2,3,4-tetraphenylbutadiene as starting material:



$M = \text{Au, Hg, B, Tl, Zr, C, Si, Sn, N, P, As, Sb, S, Se, Te.}$

R and N depend on the nature of M , but often $R = \text{phenyl}$

The present author decided to attempt to prepare pentaphenyliodole by the following reaction:



No pure compounds were isolated from the reaction mixture. It is possible that the undesirable side reaction in the preparation of the organometallic compound, which gives rise to 1,2,3-triphenylnaphthalene after quenching with water, is the cause of this result (36, 39).

SECTION 2

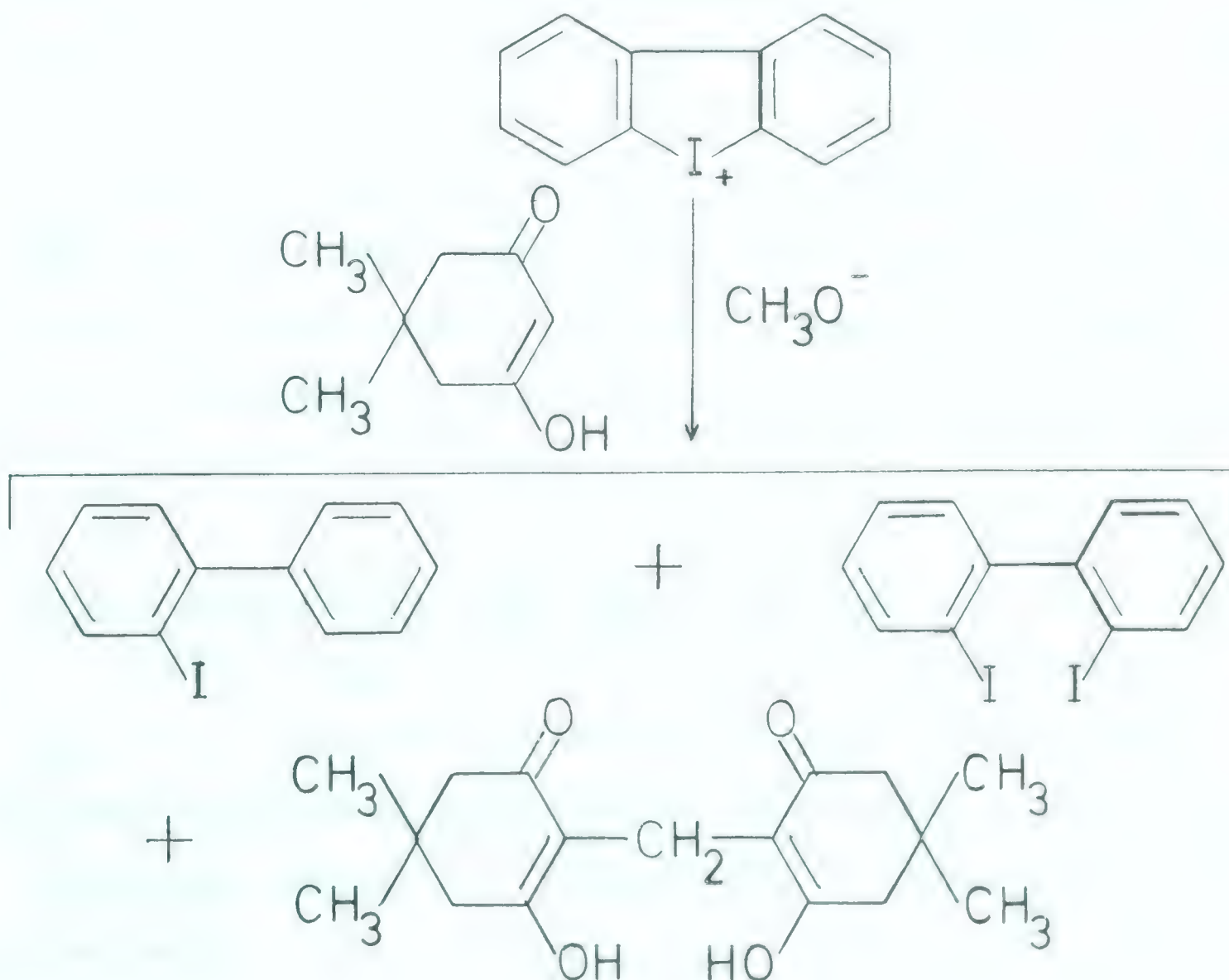
RESULTS AND DISCUSSIONS

Part II

Decomposition of Dibenziodolium Salts in Alcoholic Solutions

A. Reactions in methanol in the presence of dimedone

When dibenziodolium iodide or sulphate was decomposed in a refluxing solution of sodium methoxide and dimedone in methanol, the dimedone derivative of formaldehyde was formed.



In the case of the iodide part of the starting material did not decompose in the time allowed and was recovered. No attempt was made to isolate other reaction products in this experiment.

From the reaction mixture of the decomposed sulphate 2,2'-diiodobiphenyl and 2-iodobiphenyl were isolated in yields of respectively 4% and 37% in addition to the formaldehyde derivative. These iodo compounds have also been isolated by Fuson and Albright (7) from the decomposition products of the sulphate in yields of 5.4% and 51.7%. These authors also reported the isolation of biphenyl (11.6%).

When it is assumed that one molecule of formaldehyde originates from the decomposition of one dibenziodolium cation the yields of its dimedone derivative are 26.5% and 26.0% for the iodide and sulphate, respectively. However, the stoichiometry of the reactions involved in the formation of formaldehyde or its derivative is unknown and the assumption is only made in order to compare the yields.

For the interpretation of these results and those still to be described it was important that the formation of aldehyde in a refluxing solution of sodium methoxide and dimedone in methanol could be ruled out. In an experiment that was carried out for that purpose no derivative of formaldehyde could be isolated.

B. Reactions in methanol in the absence of dimedone

Because it might be argued that the presence of dimedone was a requisite for the formation of formaldehyde in the experiments that have been described, it was necessary to repeat the decomposition of dibenziodolium sulphate in a refluxing solution of sodium methoxide in methanol.

Because any formaldehyde that was formed in the reaction mixture would probably react rapidly in one or more ways, giving condensation and Cannizzaro reactions in the solution of sodium methoxide, the isolation of formaldehyde was expected to be difficult (40a).

Prolonged refluxing of the reaction mixture followed by an attempt to isolate the aldehyde did not seem to be a good method. Therefore it was decided to try to remove some of the aldehyde by distillation as it was produced.

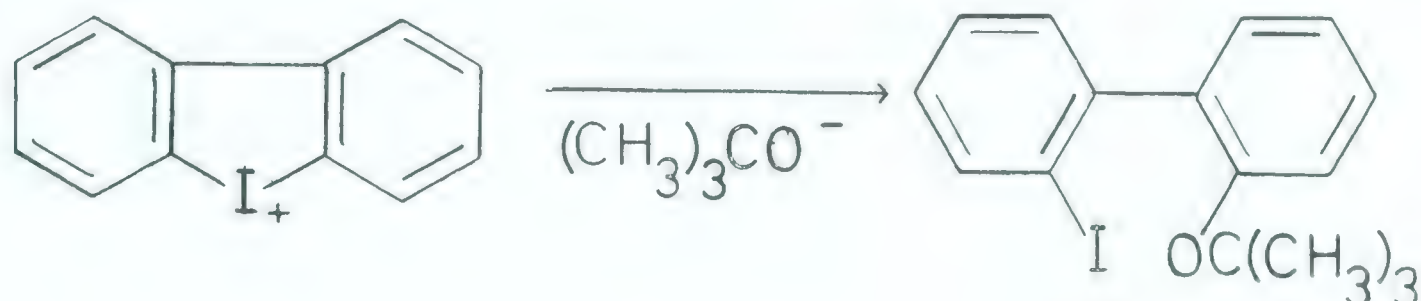
Distillation of formaldehyde from its solutions in polar solvents such as water or methanol is an inefficient process because the partial pressure of the aldehyde over its solution is low even at the boiling point (40b, 40c). However, as only the presence of formaldehyde had to be demonstrated and no quantitative determination was necessary this was not too serious a difficulty.

Distillation from a boiling solution of sodium methoxide in methanol was started immediately after the dibenziodolum sulphate had been added. Methanol was added dropwise to the reaction mixture at the same rate as the distillate was collected. In contrast to the negative reaction that the reagent-grade methanol, which was used in these experiments, gave with Tollens' reagent, a sample of the distillate gave a clearly positive reaction. This indicated the presence of reducing material and by the use of a procedure for the quantitative determination of formaldehyde (41a) it was possible to isolate a small quantity of the dimedone derivative of formaldehyde from the distillate.

When a solution of sodium methoxide in methanol was distilled in the same manner the distillate gave no reaction with Tollens' reagent, which indicated the absence of formaldehyde.

C. Reaction in tertiary butyl alcohol

When the decomposition of dibenziodolium sulphate was carried out in t-butyl alcohol containing sodium t-butoxide a high-boiling liquid could be isolated. On the basis of analysis and its infrared spectrum (see Fig. 1) the structure of 2-iodo-2'-t-butoxybiphenyl has been assigned to it.



The infrared spectrum shows absorption bands that can be attributed to aromatic C-H stretching vibrations (3060 cm^{-1}), aliphatic C-H stretching vibrations (2980 and 2875 cm^{-1}) in $-CH_3$ (42a), C-H deformation vibrations of o-disubstituted phenyl (753 cm^{-1}), and skeletal stretching vibrations of a conjugated aromatic system (1598 and 1578 cm^{-1}). A split band with peaks at 1385 and 1360 cm^{-1} , the latter having approximately twice the intensity of the first, can be attributed to the deformation vibrations of C-H in the t-butyl group (42b). Finally, the C-O stretching vibrations of an aralkyl ether probably cause the absorption peaks at 1250 and 1150 cm^{-1} , of which the latter has a great intensity (42c).

For purposes of characterization an attempt was made to prepare 2-iodo-2'-t-butoxybiphenyl by another method. Stevens (43) reported the preparation of t-alkyl aryl ethers with satisfactory yields by passing through isobutene in the appropriate phenol in the presence of a trace of sulphuric acid. He found that in general nuclear alkylation increased at

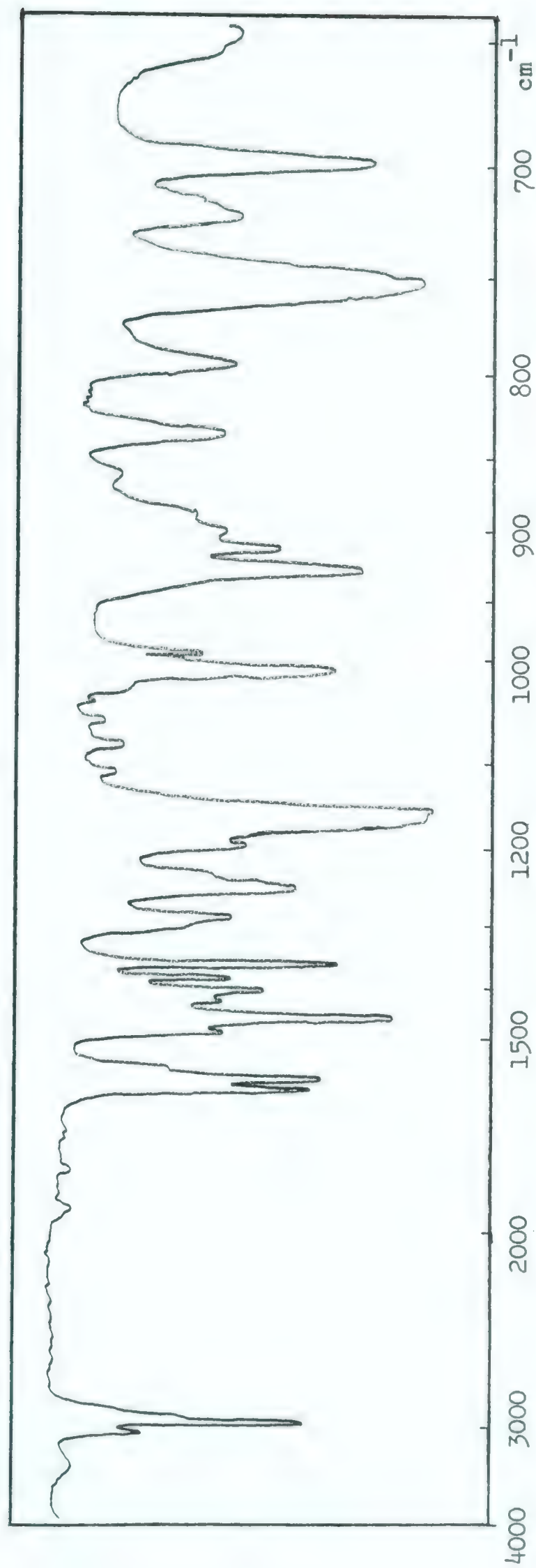
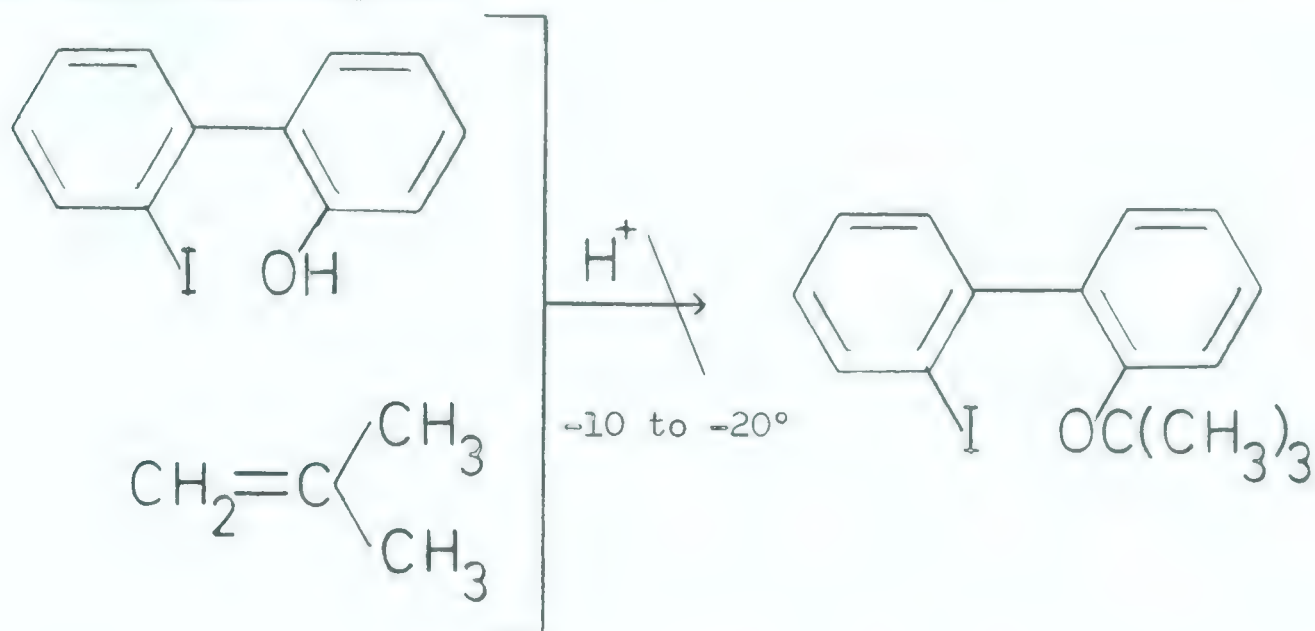


Fig. 1. Infrared absorption spectrum of 2-iodo-2'-t-butoxybiphenyl.

Liquid film; Perkin Elmer 21.

the expense of ether formation when the temperature or concentration and amount of acid catalyst were increased.

As isobutene at -10° could be used as solvent for solid phenols that method was adopted.



The starting material 2-iodo-2'-hydroxybiphenyl was recovered unchanged, however, and the attempt was a failure.

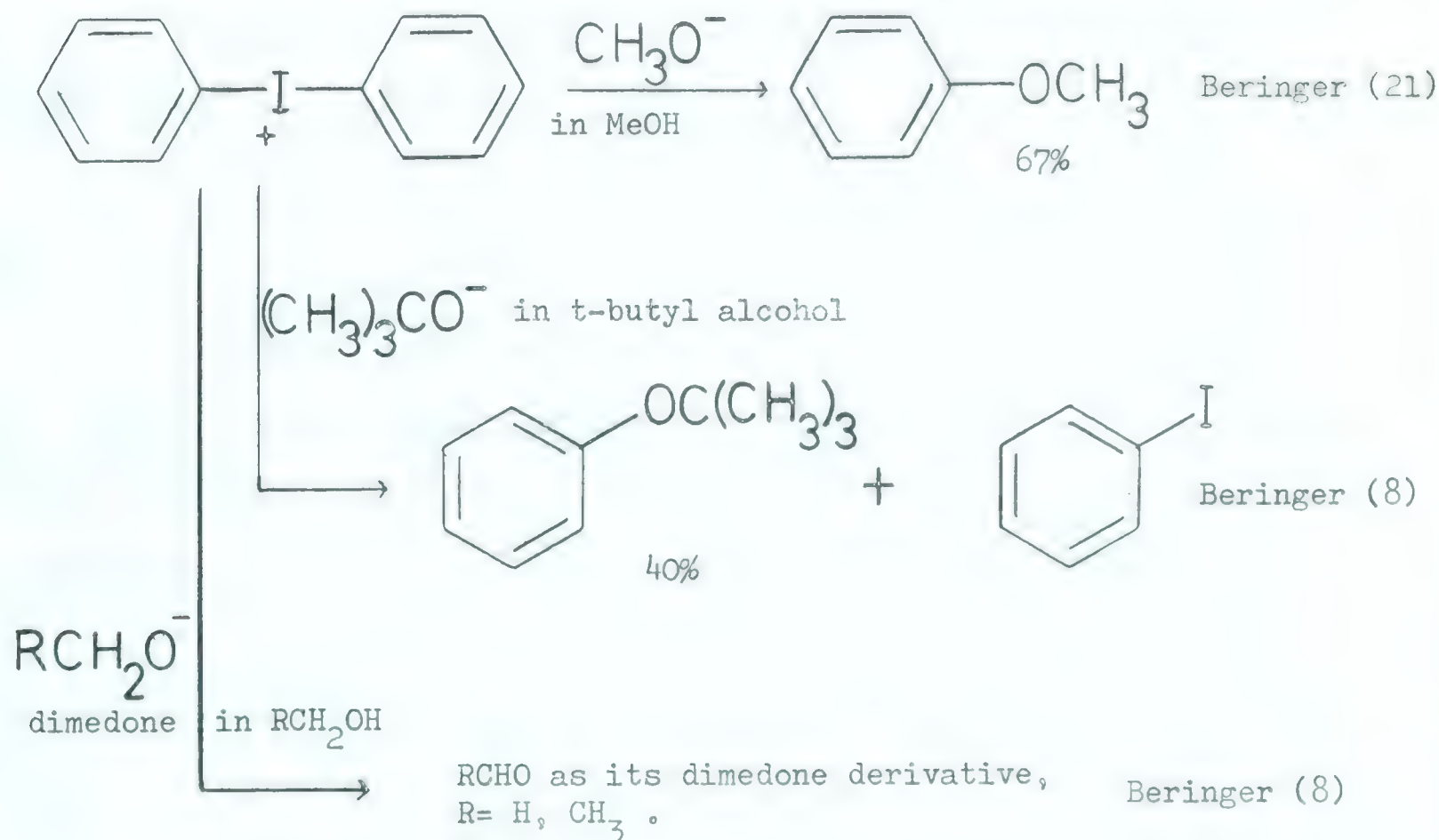
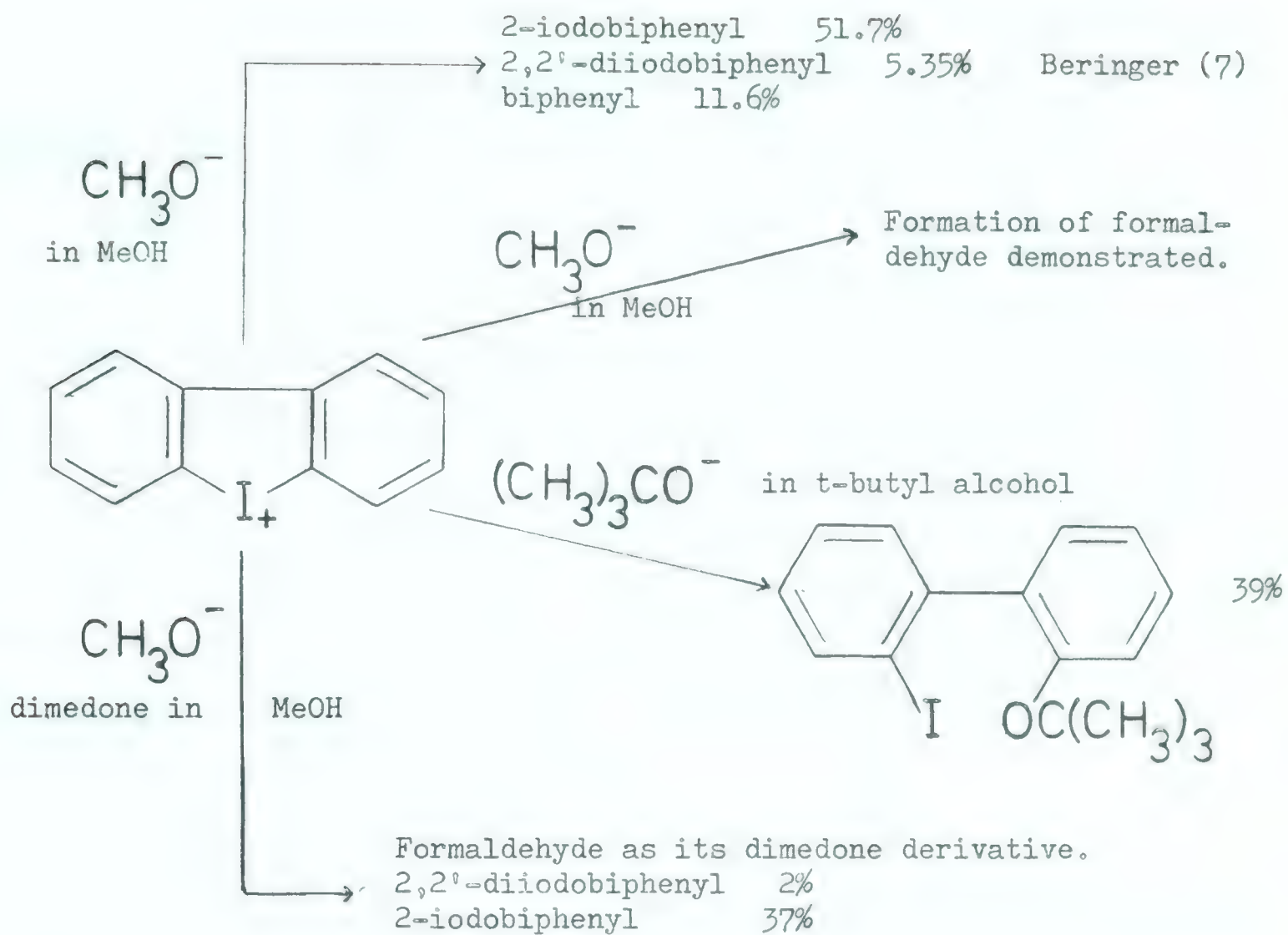
D. Discussion

It is interesting to compare the present results with those obtained by Beringer and co-workers (8, 21) in their work with diphenyliodonium salts.

Any explanation of the combined results of which a schematic review is given on the next page will have to satisfy the following observations:

1. In contrast to the reaction of the diphenyliodonium cation with methoxide anion (21), which gave rise to the "normal" product anisole, the same reaction with dibenziodolium salt gave no methyl ether but biphenyl and two derivatives which contained iodine (7).

2. The decomposition of both iodonium salts with methoxide and dimedone in methanol was accompanied by dehydrogenation of the solvent

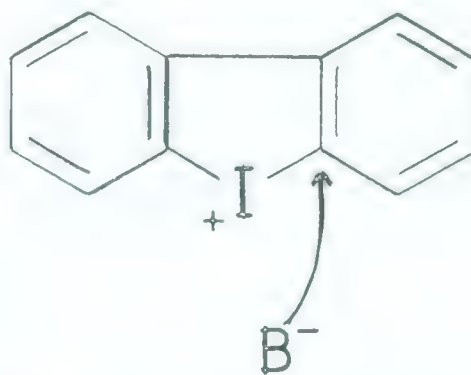


to formaldehyde, which was isolated as its dimedone derivative.

3. When no dimedone was present the decomposing dibenziodolium salt caused dehydrogenation, but the diphenyliodonium compound gave the expected anisole.

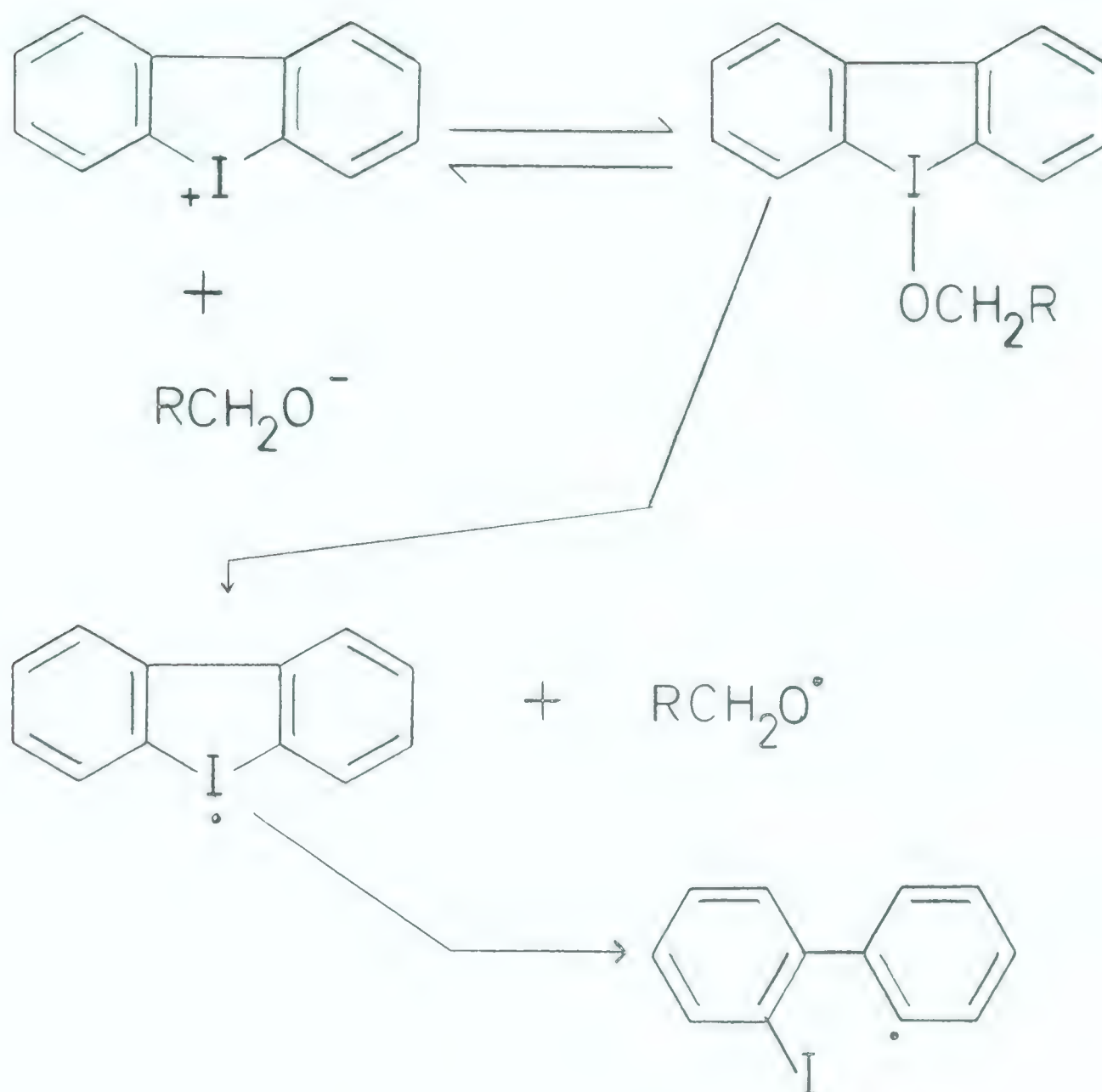
4. With t-butoxide both compounds gave the t-butyl ether.

The following is an attempt to rationalize these results. If it is assumed that a tetrahedral arrangement, or nearly so, exists at the carbon atom under attack in the transition state in a nucleophilic aromatic substitution (44), such a substitution for iodine on carbon and opening of the central ring of the dibenziodolium cation would involve a twisted



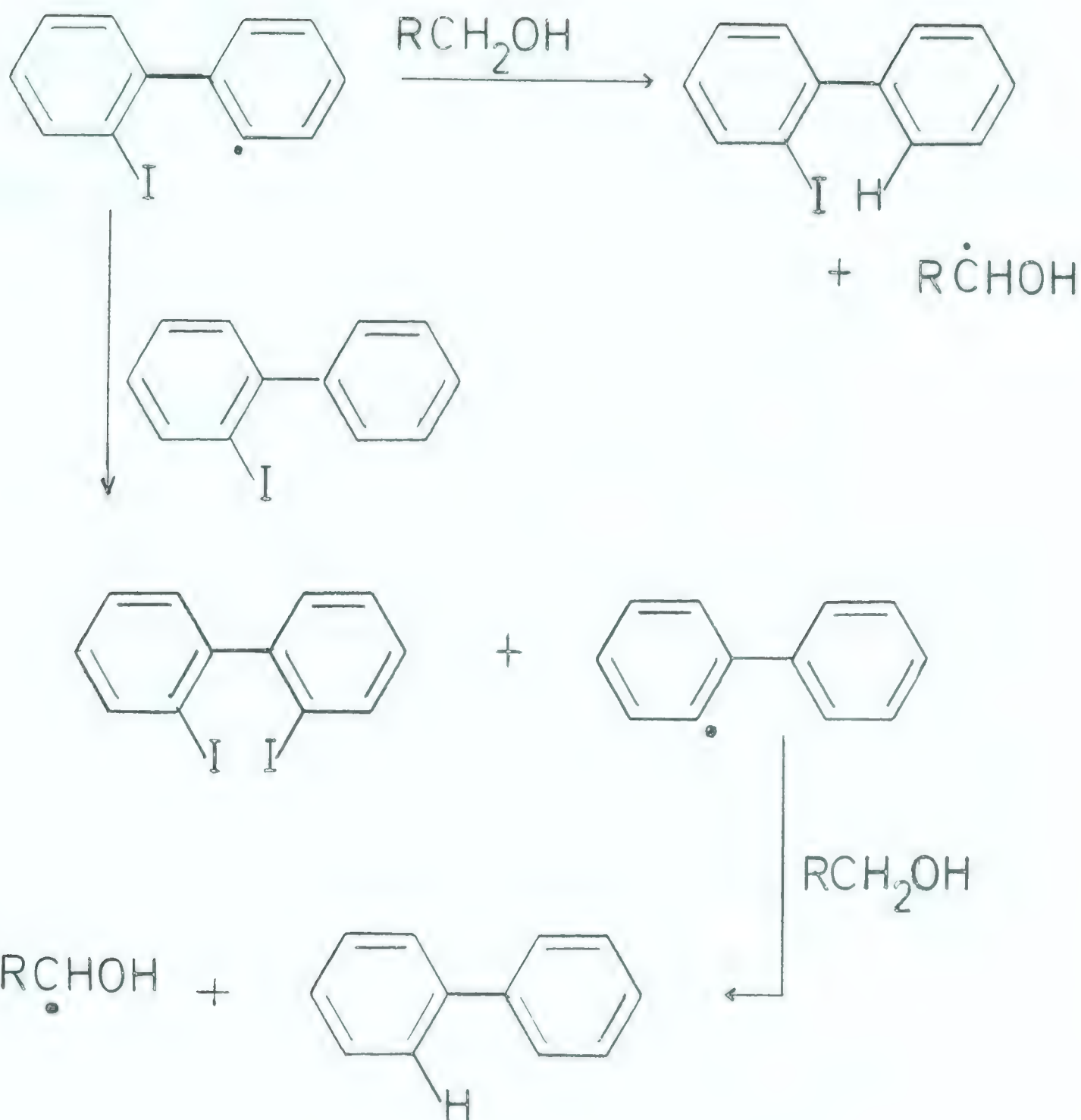
molecule and loss of coplanarity of the two phenyl rings in the transition state. This would explain that nucleophilic displacement is favoured in the case of the diphenyliodonium cation and that anisole and t-butyl phenyl ether are formed without difficulty.

The other reactive site in the two iodonium cations under discussion is the iodine atom. The present author interprets the formation of aldehyde as a result of dehydrogenation of the solvent by radicals which are produced when a covalent intermediate decomposes. In the case of the dibenziodolium ion the reaction sequence as outlined on the next page is suggested.



The following explanation of the formation of the products is speculative. The 2-iodobiphenyl radical might react with the substrate $\text{R-CH}_2\text{OH}$ or with 2-iodobiphenyl leading to the formation of 2-iodobiphenyl, 2,2'-diiodobiphenyl and a biphenyl radical, which might again react with the substrate.

This sequence of reactions would account for the products that were isolated by Fuson and Albright (7), and leads to the formation of $\text{CH}_3\text{O}^\bullet$ and $^\bullet\text{CH}_2\text{OH}$ when the reaction is carried out in methanol.



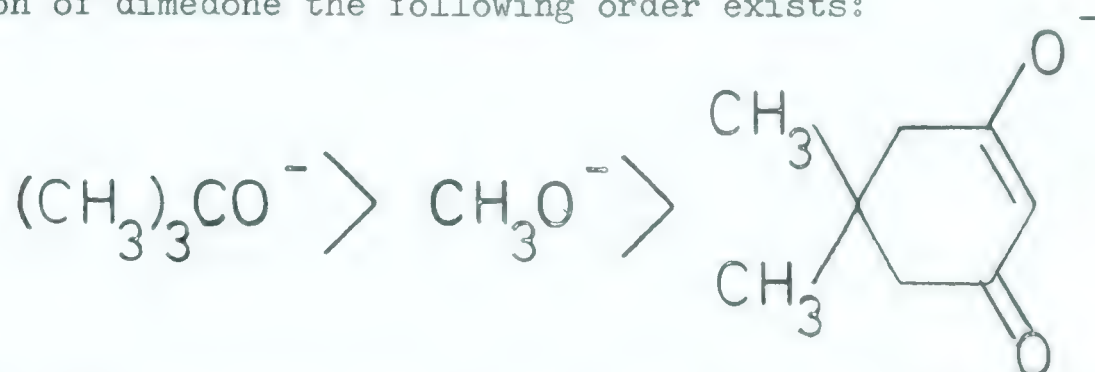
Probably the following reaction would occur:



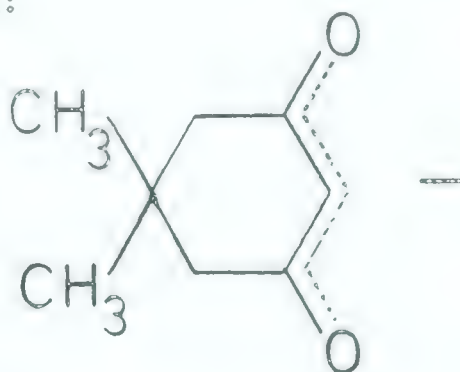
and formaldehyde might be formed as a result of abstraction of a hydrogen atom by a radical species:



Dimedone with a pK_a 5.2 (45) has an acidity comparable with that of an aliphatic carboxylic acid. Therefore the anion of dimedone and the methoxide anion is present in the reaction mixtures containing dimedone. For the basicity of the t-butoxide and methoxide anions and the anion of dimedone the following order exists:

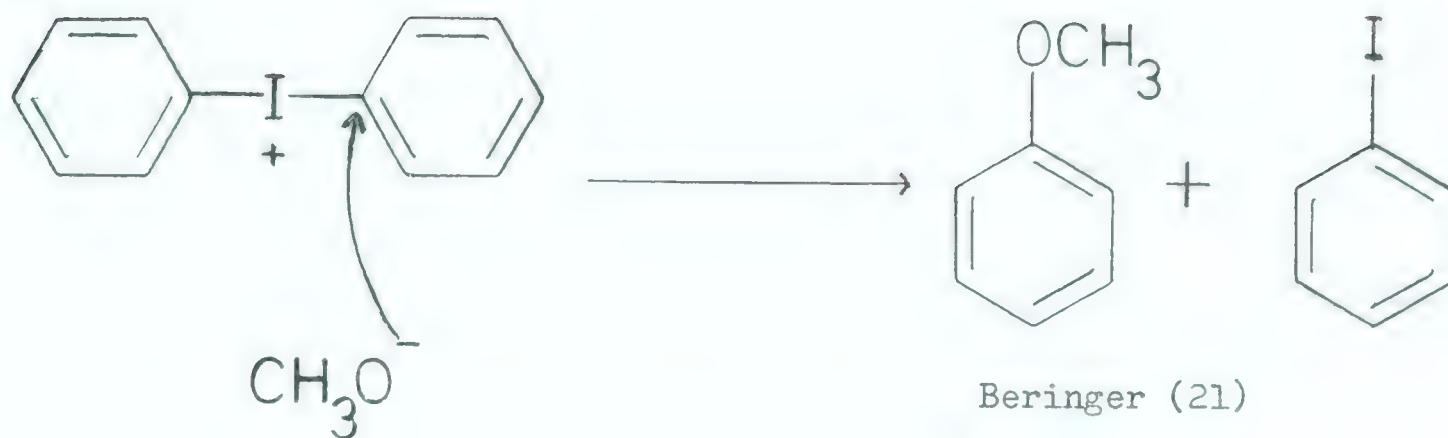


For nucleophilicity the same order would be expected because for the same atom at the nucleophilic center the nucleophilicity can normally be correlated with the basicity of the nucleophilic reagent (46). However, the anion of dimedone is radically different from the alkoxide anions and should be a weaker nucleophile than expected on the basis of its basicity. This is because the negative charge in the resonance stabilized anion is delocalized:

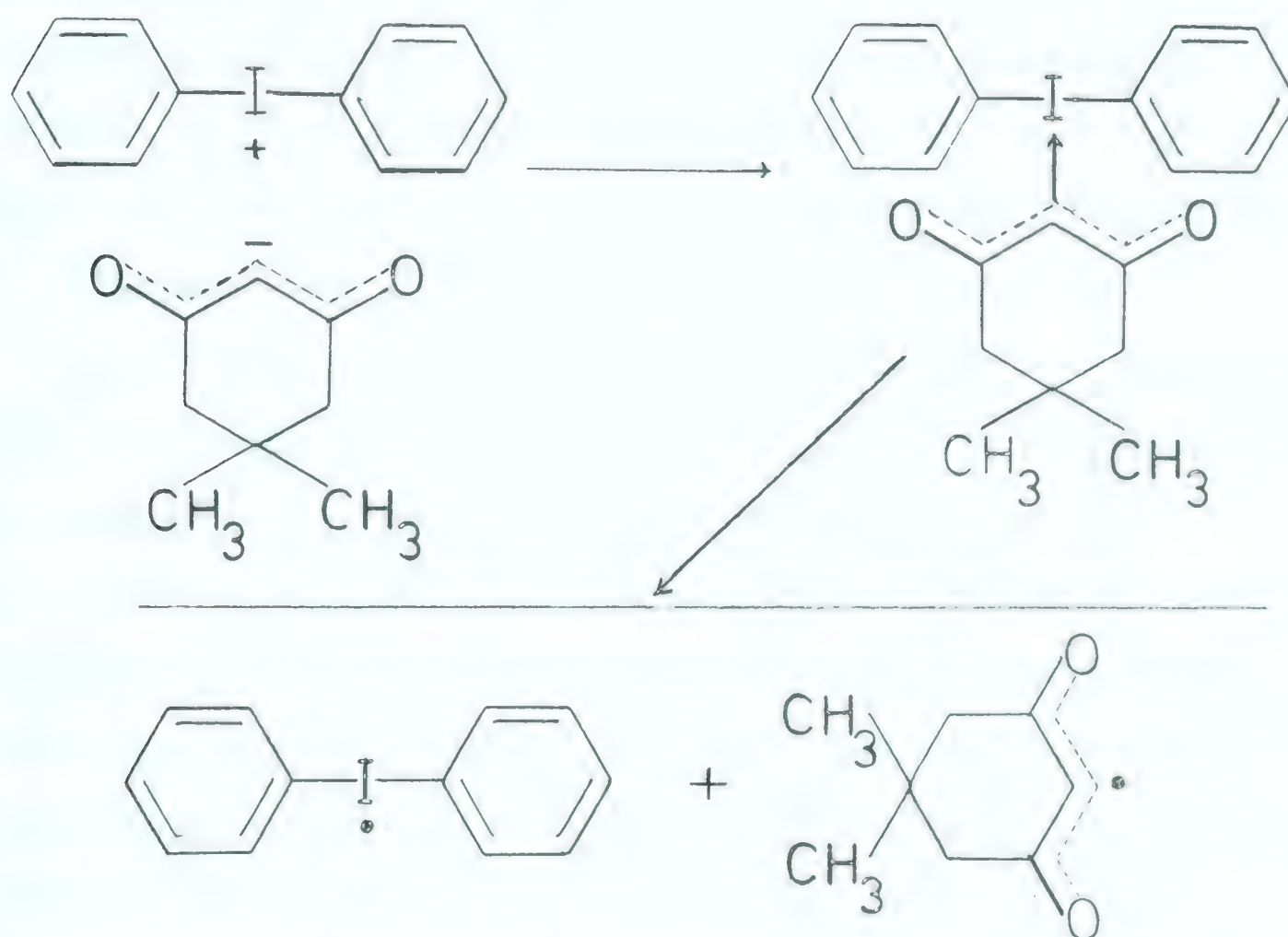


Because the negative charge is dispersed solvation is expected to be less than in the case of the methoxide anion and the polarizability of the delocalized π electron system is probably greater.

Both these factors explain why a covalent bond might be formed. This in turn would explain the decomposition of the diphenyliodonium salt in a solution of the dimedone anion in methanol. It would also explain the formation of anisole when no dimedone is present. In this case nucleophilic substitution occurs:



but in the presence of dimedone:



After decomposition of the covalent compound has occurred the radicals may dehydrogenate the solvent methanol giving rise to formaldehyde or its derivative by one or more of the possible pathways.

The above work has lead to the successful preparation of the salt the dibenziiodolium cation and the dimedone anion. This salt which was found to have interesting properties is discussed in Part III of Section 2.

SECTION 2

R E S U L T S A N D D I S C U S S I O N S

P a r t I I I

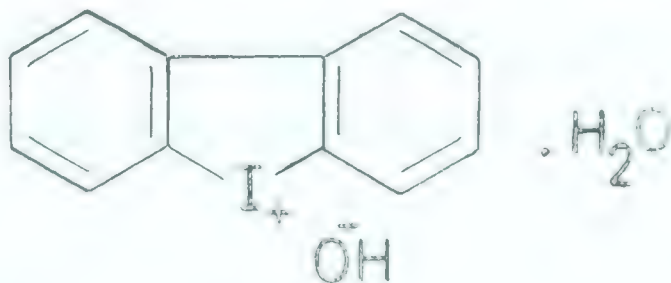
Some New Dibenziodolium Compounds

A. Dibenziodolium hydroxide monohydrate

In the course of the present investigations it was discovered that when a solution of sodium hydroxide was added to a hot aqueous solution of dibenziodolium sulphate the mixture turned yellow and that fine colourless crystals appeared when the solution was cooled.

Although it seemed likely that the hydroxide was isolated, it was on the other hand a surprise because no solid iodonium hydroxides had been reported in the literature. Solutions containing the hydroxides had usually been prepared by shaking suspensions of the halides in water with silver oxide. This way Mascarelli and Gatti (18) had obtained a solution containing dibenziodolium hydroxide from which they isolated a yellow material that as a result of an analysis was thought to be a mixture of the hydroxide and the bicarbonate.

In the present work the colourless hydroxide was isolated as a monohydrate, which could be dried at 75° to a brownish yellow anhydrous compound.



The infrared spectrum of the monohydrate is reproduced in Fig.2 . It shows the absorptions of a dibenziodolium salt, which are all rather weak except for the strong absorption at 745 cm^{-1} that can be assigned to the C-H deformation vibrations of an o-disubstituted phenyl group. In the region from $3500\text{--}3050\text{ cm}^{-1}$ there is a broad absorption of intermediate intensity which together with the absorption at $1650\text{--}1600\text{ cm}^{-1}$ is caused by the water of hydration.

There is one strong absorption at 1320 cm^{-1} , close to one of the peaks caused by the mineral oil in the sample, for which the present author has no explanation. At first it was thought to be caused by the presence of a phenol (42d) in the sample. However, by comparison with the spectrum of 2-iodo-2'-hydroxybiphenyl it became evident that this compound was not present as an impurity. Phenol itself can not be the impurity either because in that case there should be an absorption band between 710 and 690 cm^{-1} for the deformation vibrations of the monosubstituted phenyl group, and there is none.

B. Dibenziodolium 5,5-dimethyl-3-keto-1-cyclohexenolate dihydrate (or the dimedate dihydrate)

As a result of work that has been described in Part II of Section 2 the present author got the idea that probably a covalent dimedate acted as an intermediate in some of the reactions.

An attempt was therefore made to prepare dibenziodolium dimedate. When a hot aqueous solution of equivalent amounts of dibenziodolium sulphate and sodium dimedate was cooled slowly the salt of dimedone crystallized as the dihydrate. It could be recrystallized from a large volume of water.

When it was heated to 50° or dried in vacuo at room temperature

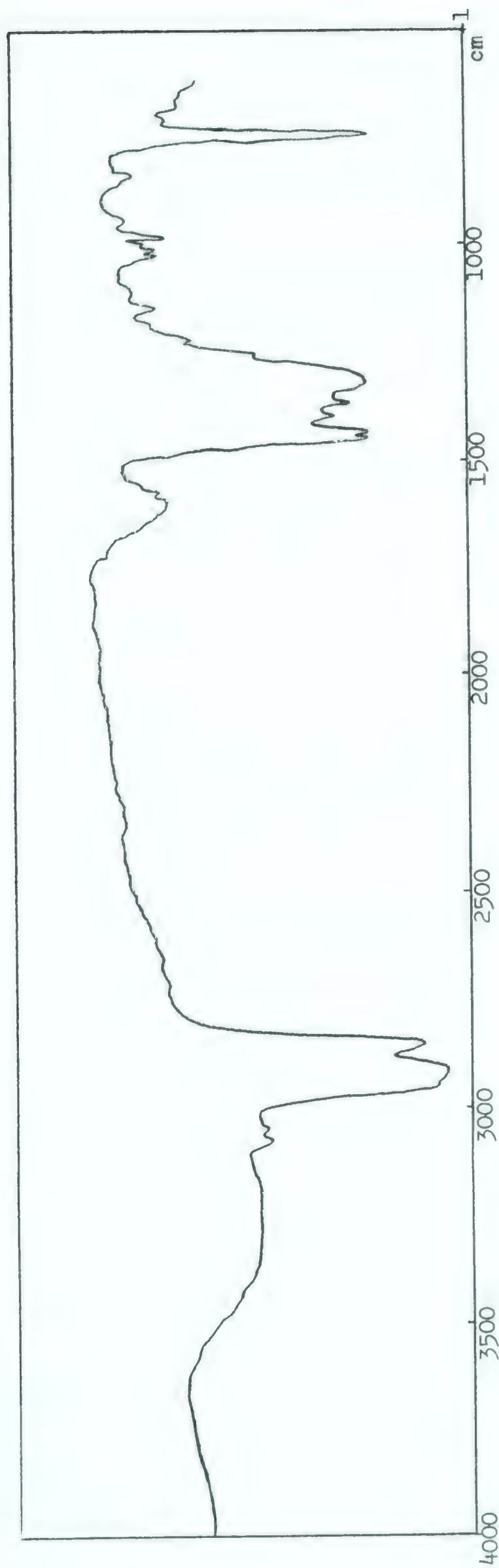


Fig. 2. Infrared absorption spectrum of dibenziodolium hydroxide monohydrate.

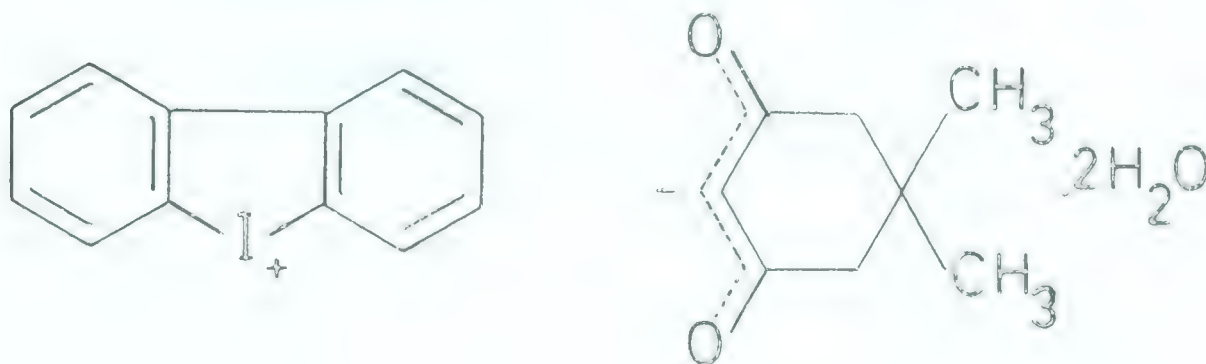
Mineral-oil mull (nujol); Perkin Elmer 221.

the salt turned yellow and the anhydrous compound was obtained.

The following equilibrium was found to exist:



The dimedate can best be represented by the following structure, which shows the resonance-stabilized anion of dimedone.



The infrared spectra of the original compound, as it crystallized from the solution, and of the hydrate, as obtained when the anhydrous compound was exposed to air, were identical. The spectrum is reproduced in Fig. 3. It shows a very broad absorption band between 3550 and 3100 cm^{-1} and a weak absorption peak at 1650 cm^{-1} , both attributed to the water of hydration. Most of the numerous weak absorption bands that are characteristic for a dibenziodolium compound can still be recognized, but the spectrum is dominated by the strong absorptions caused by the dimedone moiety of the molecule with its maximum at 1500 cm^{-1} .

Neilands and Vanags (47) found that the enolate anion system of dimedone caused an extremely intense absorption in the region 1530-1510 cm^{-1} , and later they reported that the sodium salt of 5-phenyl-1,3-cyclohexanedione and the silver salt of 2-iodo-5-phenyl-1,3-cyclohexanedione absorbed intensely at respectively 1520 cm^{-1} and at 1490-1450 cm^{-1} (48).

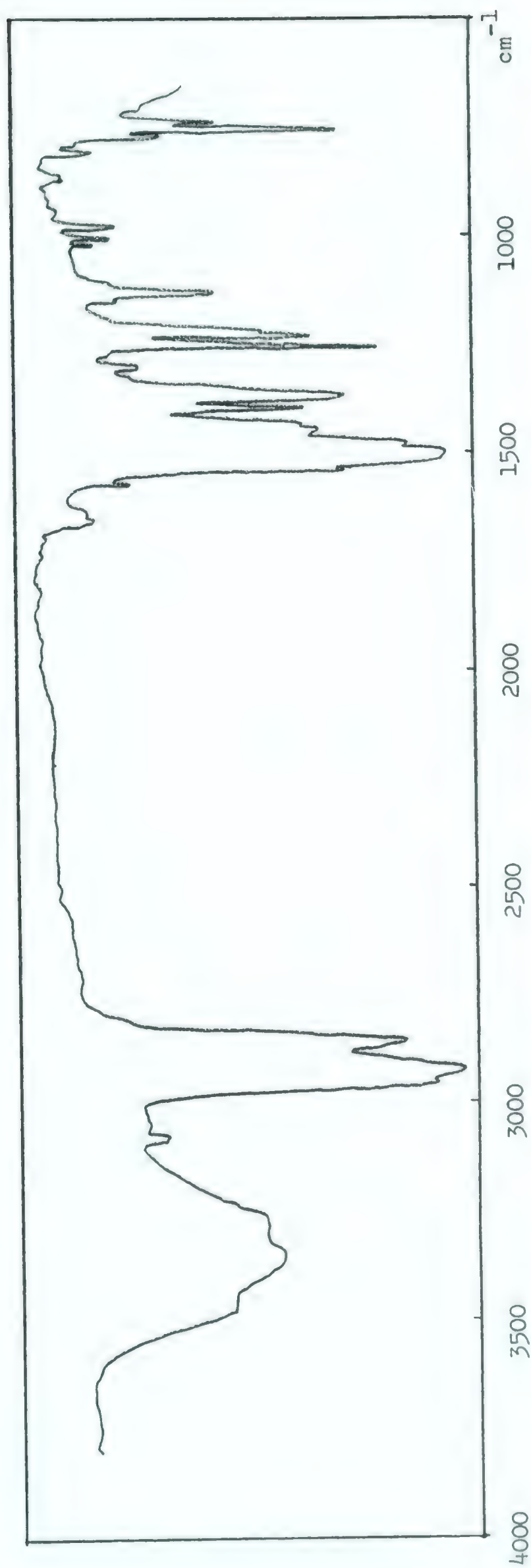


Fig. 3. Infrared absorption spectrum of dibenziodolium 5,5-dimethyl-3-keto-1-cyclohexenolate dihydrate (the dimedate dihydrate).
Mineral-oil mull (nujol); Perkin Elmer 221.

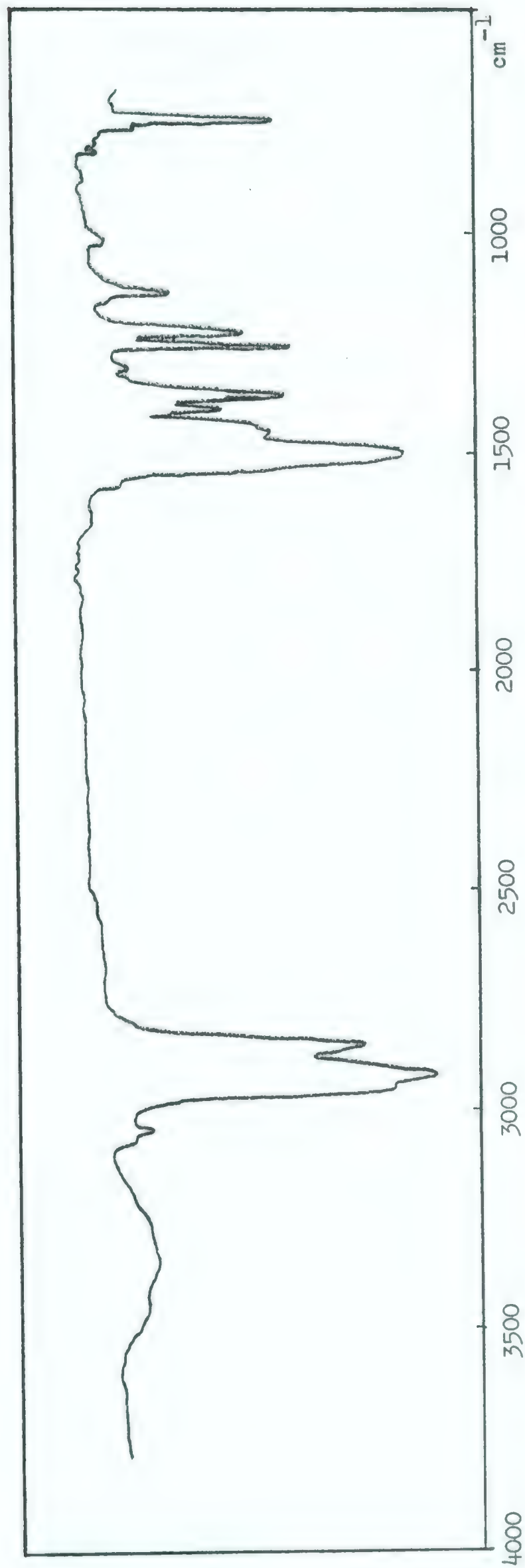


Fig. 4. Infrared absorption spectrum of dibenziodolium 5,5-dimethyl-3-keto-1-cyclohexenolate (the anhydrous dimedate).
Mineral-oil mull (nujol); Perkin Elmer 221.

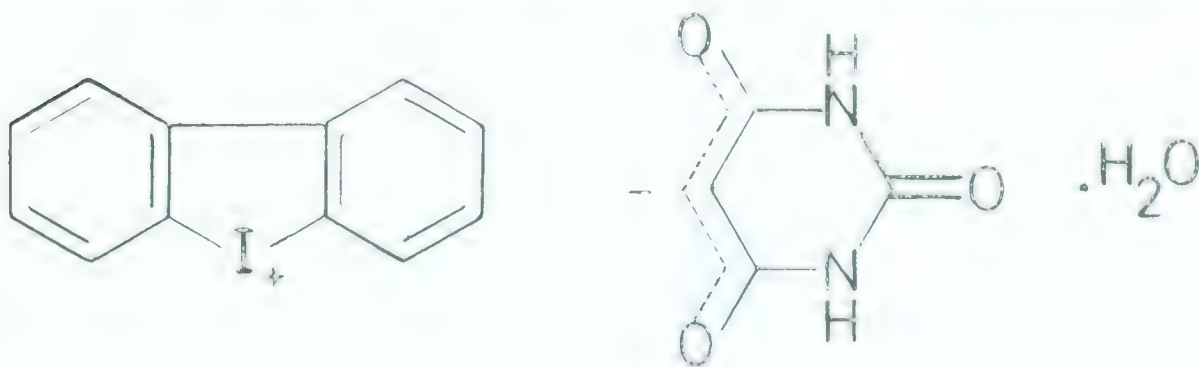
In the infrared spectrum of the yellow anhydrous compound (Fig.4) the absorptions attributed to the water of hydration are not present any more. The strong absorption band at 756 cm^{-1} in the spectrum of the hydrate has almost disappeared, but an absorption at 740 cm^{-1} , which is weak in the spectrum of the hydrate, has a much increased intensity in the case of the anhydrous compound. The present author has no explanation for these changes.

C. Dibenziodolium barbiturate monohydrate

Because the dibenziodolium salt obtained from dimedone had such an interesting property, the barbiturate was prepared because the anion has a structure similar to that of dimedone. It was hoped that it would also exhibit a colour change when it was dried.

When a solution of sodium barbiturate was added to a solution of dibenziodolium sulphate a colourless crystalline precipitate was formed immediately. By analysis it was found to be the monohydrate of the barbiturate. This compound had a very low solubility in water. When a solution of potassium iodide was added to the mother liquor from which the barbiturate had been isolated, there was only a faint turbidity indicating that it is almost as insoluble as dibenziodolium iodide.

The compound may be represented by the following structure:



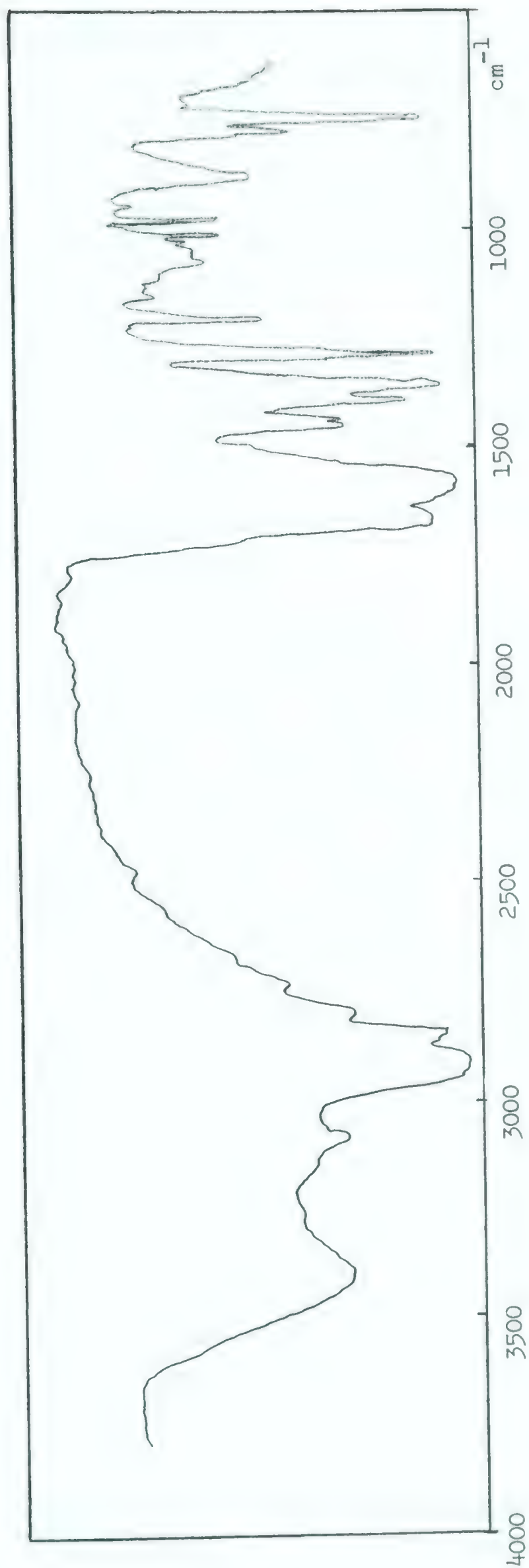


Fig. 5. Infrared absorption spectrum of dibenziodolium barbiturate monohydrate.

Mineral-oil mull (nujol); Perkin Elmer 221.

When a sample of the monohydrate was placed on a watch glass in a vacuum desiccator it visibly turned yellow in two minutes after the vacuum (1-5 mm.) had been established. For analysis it was dried at 70° to constant weight; again the yellow colour appeared.

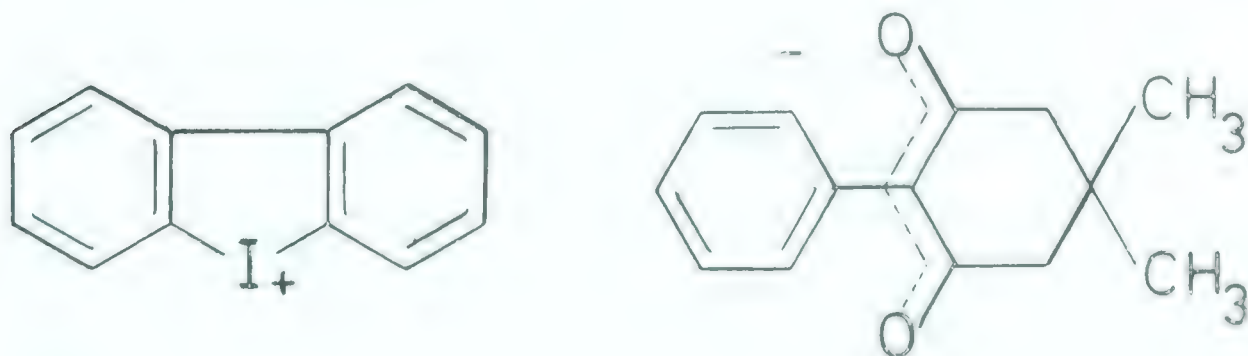
The infrared spectrum of the hydrate, reproduced in Fig. 5, shows a strong broad absorption with its maximum intensity at 3413 cm^{-1} , which is not present any more in the spectrum of the anhydrous material. The many small absorption peaks of a dibenziodolium salt are present.

D. Dibenziodolium 5,5-dimethyl-2-phenyl-3-keto-1-cyclohexenolate (or the 2-phenyldimedata)

For reasons which will be discussed later it seemed interesting to prepare the dibenziodolium salt of 2-phenyldimedone.

The same method of preparation was used as for the dimedata and barbiturate. The bright yellow product precipitated immediately from the hot solution, being very insoluble in water. It contained no water of hydration and it was soluble in methanol, ethanol, dimethyl sulphoxide, and chloroform; yellow solutions were formed.

Its infrared spectrum (Fig.6) showed no absorption in the region $3500\text{--}3100\text{ cm}^{-1}$. The very strong absorption at 1455 cm^{-1} can not be attributed to mineral oil (nujol) only, but may be caused by the phenyl-substituted resonance-stabilized anion of 2-phenyldimedone:



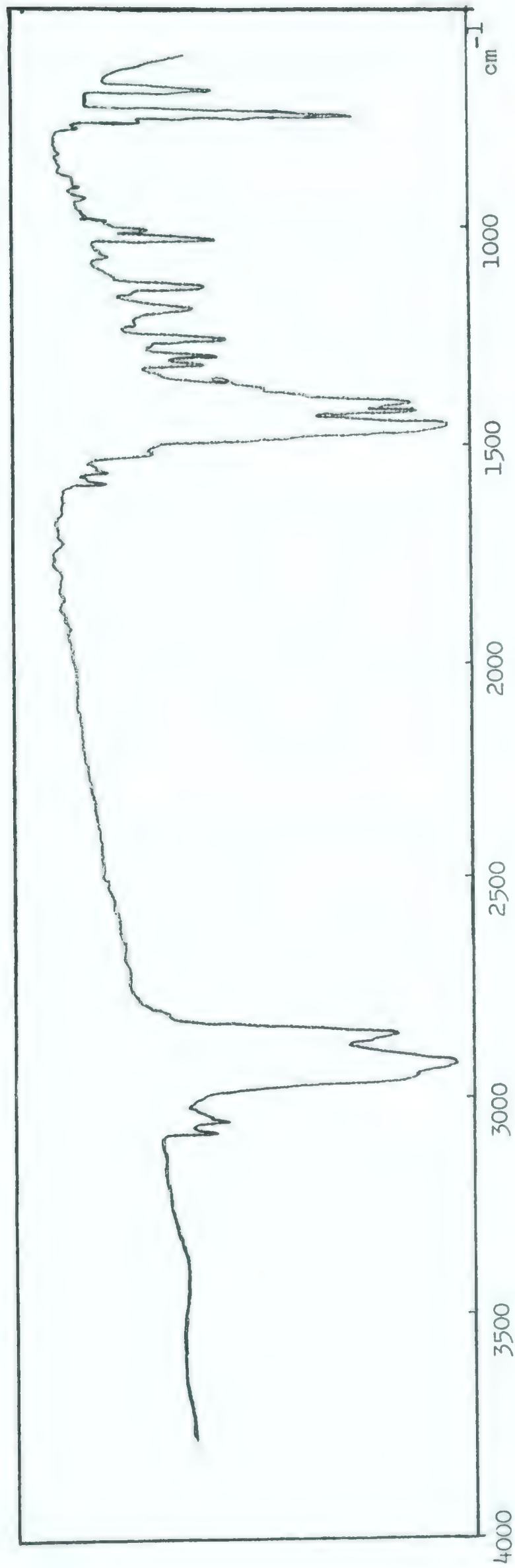


Fig. 6. Infrared absorption spectrum of dibenziodolium 5,5-dimethyl-2-phenyl-3-keto-1-cyclohexenolate (the 2-phenyldimedata).
Mineral-oil mull (nujol); Perkin Elmer 221.

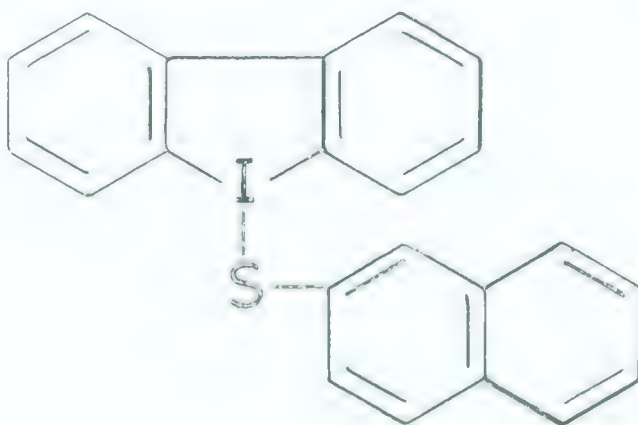
As mentioned earlier, Neilands and Vanags (48) found intense absorption at $1490\text{--}1450\text{ cm}^{-1}$ in the spectrum of the silver salt of 2-iodo-5-phenyl-1,3-cyclohexanedione.

E. Dibenziodolium 2-naphthalenethiolate

In a search for a stable iodonium thiolate it was found that a bright yellow precipitate was obtained immediately when a solution of sodium 2-naphthalenethiolate was added to a solution of dibenziodolium salt.

In contrast to the benzenethiolate, which previously had been found to decompose rapidly, this compound was stable. The reason why so much interest was taken in these compounds in the present investigations was the fact that unstable yellow sulphides and thiolates had been involved in several reactions where radicals seemed to be intermediates (5,6).

The dibenziodolium 2-naphthalenethiolate has been the subject of several decomposition experiments in various solvents which are described in Part IV of Section 2. Mainly as a result of evidence obtained in these experiments and as a result of the nature of the ultraviolet spectrum of the thiolate, which will be discussed later, the compound is regarded covalent:



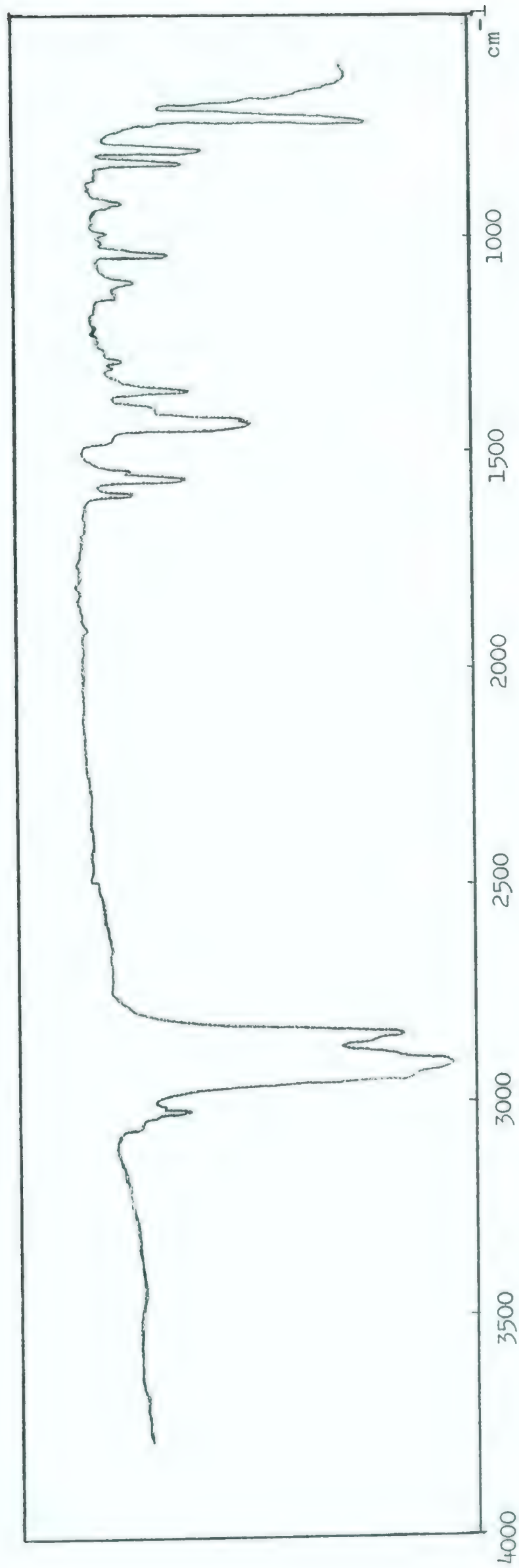


Fig. 7. Infrared absorption spectrum of dibenziodolium 2-naphthalenethiolate.
Mineral-oil mull (nujol); Perkin Elmer 221.

The infrared spectrum has been reproduced in Fig. 7; it shows the absorption peaks that can be assigned to the dibenziodolium and 2-naphthyl moieties.

F. The structure of the new dibenziodolium compounds

Of the five dibenziodolium salts which have been described in the preceding pages the two anhydrous compounds are brightly yellow and the three hydrates are colourless; the latter can be dried and give yellow products.

It is tempting to explain the colour of the anhydrous compounds as resulting from the formation of a covalent bond. Unfortunately the present author can not present conclusive evidence for a covalent bond that is formed when the water of hydration is removed by drying. All efforts to collect spectral evidence for covalency have been fruitless, probably because traces of moisture in the solvent are already sufficient to cause the covalent bond to change into an ionic bond. This shows up in the ultraviolet spectra as an absorption at 263-265 $m\mu$, which is characteristic for the dibenziodolium cation (49).

The formation of an unstable covalent iodonium hydroxide has been suggested by Caserio, Glusker, and Roberts (17) and some of the results obtained in the decomposition of iodonium compounds in alcoholic solutions, as described in the preceding Part II of Section 2, can be rationalized by the assumption that a dimedate plays a role.

More successful has been the investigation of the ultraviolet spectrum of the 2-naphthalenethiolate. With 95% ethanol as solvent the spectrum showed continuous absorption between 214 and 300 $m\mu$ with a small shoulder at 249 $m\mu$. Contrasting with this is the absorption peak at 263 $m\mu$ ($\log \epsilon \sim 4.00$) that is shown by solutions of dibenziodolium

chloride or tosylate in 95% ethanol or methanol.

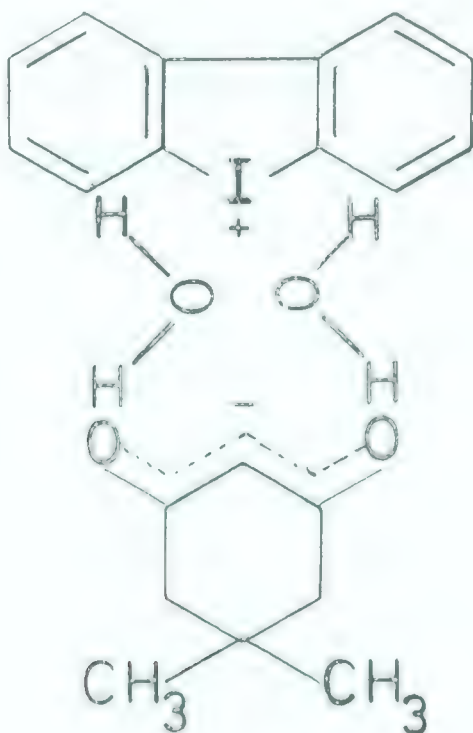
That the different spectrum of the 2-naphthalenethiolate in ethanol was not a result of rapidly decomposed material was shown by comparison with the spectrum taken of a solution of the thiolate in ethanol which had been allowed to decompose for 24 hours.

The 2-naphthalenethiolate anion was found to give high-intensity absorption at 263, 297, and 307 $m\mu$ in ethanol (50).

When dissolved in dimethyl sulphoxide the 2-naphthalenethiolate gave a maximum absorption at 364 $m\mu$ ($\log \epsilon$ 4.00) which is not shown by a solution of the tosylate in the same solvent. The tosylate shows a maximum at 266 $m\mu$ ($\log \epsilon$ 3.9).

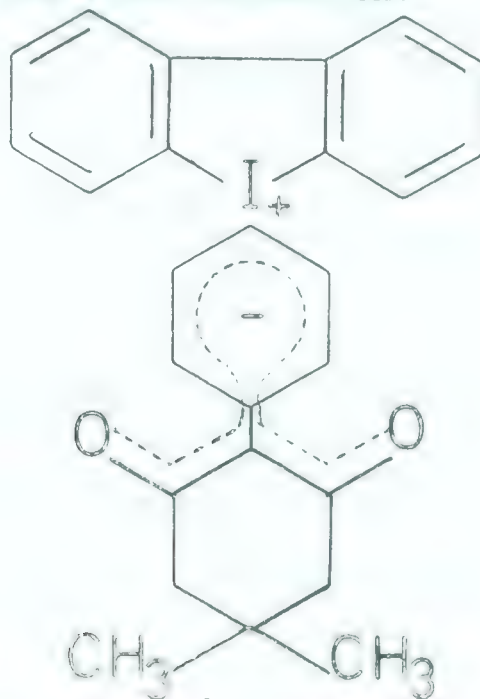
These data are considered evidence for the absence of the dibenziodolium cation and the presence of a covalent iodine - sulphur bond in the 2-naphthalenethiolate.

The smooth reversible transition from hydrate to anhydrous compound accompanied by change in colour has given rise to much thought about a possible formation of a solvent-separated ion pair in the solid state. However, this is just a possibility and there is no evidence for it whatsoever. When dibenziodolium dimedate dihydrate was prepared and its change of colour was noted, the following arrangement was considered to be a possibility:



In the anhydrous compound there might be some direct interaction between the iodine atom and the delocalized π orbital system of the anion.

The 2-phenyldimedata was prepared because the bulky phenyl group might be expected to interfere with this interaction, keeping the iodine atom and the π orbital system apart, or rather, being itself part of this system, changing the whole situation:



It is interesting that the 2-phenyldimedata contains no water of hydration and that the barbiturate forms only a monohydrate. However, coplanarity of the dibenziodolium cation and the anion is not the only arrangement that is possible. Quite conceivably, as an alternative the anion and cation could be located in two parallel planes, or even in planes at an angle.

Important for the steric structure of any covalent iodonium compound would be the type of hybridization of the iodine atom.

SECTION 2

R E S U L T S A N D D I S C U S S I O N S

P a r t I V

Decomposition of Dibenziodolium 2-Naphthalenethiolate in Various Solvents

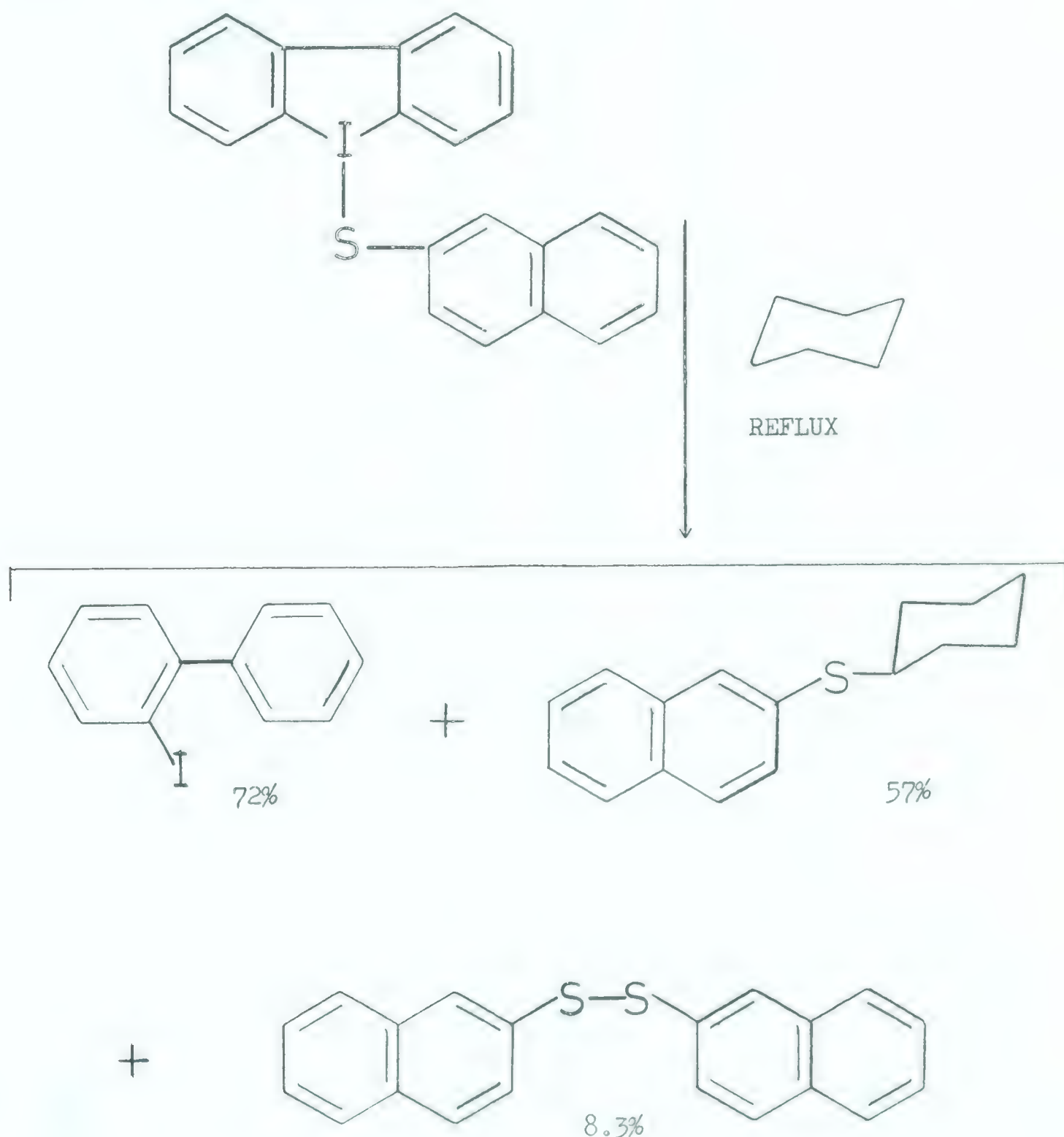
The yellow dibenziodolium 2-naphthalenethiolate of which the preparation has been described in Part III of Section 2 was insoluble in water and very slightly soluble in ethanol. In preliminary small-scale tests it was found that the compound decomposed fairly rapidly in pyridine, dimethyl sulphoxide, toluene, benzene, and tetrahydrofuran at room temperature.

At first it was thought that no decomposition took place in cyclohexane and that this solvent could be used to extract any 2,2'-dinaphthyl disulphide that might be present in the thiolate. This was before it was shown by analysis that the "crude" thiolate was pure. When cyclohexane was used for this purpose and a suspension of the 2-naphthalenethiolate in this solvent was heated to reflux, rapid decomposition occurred. In the mean time experiments in tetrahydrofuran and carbon tetrachloride were started on a larger scale.

A. Decomposition in cyclohexane

In terms of isolation and identification of products the decomposition in cyclohexane was more successful than the decomposition in other solvents.

All decompositions in cyclohexane were carried out by stirring a suspension of dibenziodolium 2-naphthalenethiolate at the temperature of reflux in a nitrogen atmosphere. The yields of 2,2'-dinaphthyl disulphide from the reaction mixture ranged from 8.3 to 14.2%. In addition an oil was obtained which contained a large quantity of 2-iodobiphenyl. Also one other compound, which was later found to be cyclohexyl 2-naphthyl sulphide was isolated. Separation of these two compounds could not be achieved by chromatography on alumina.



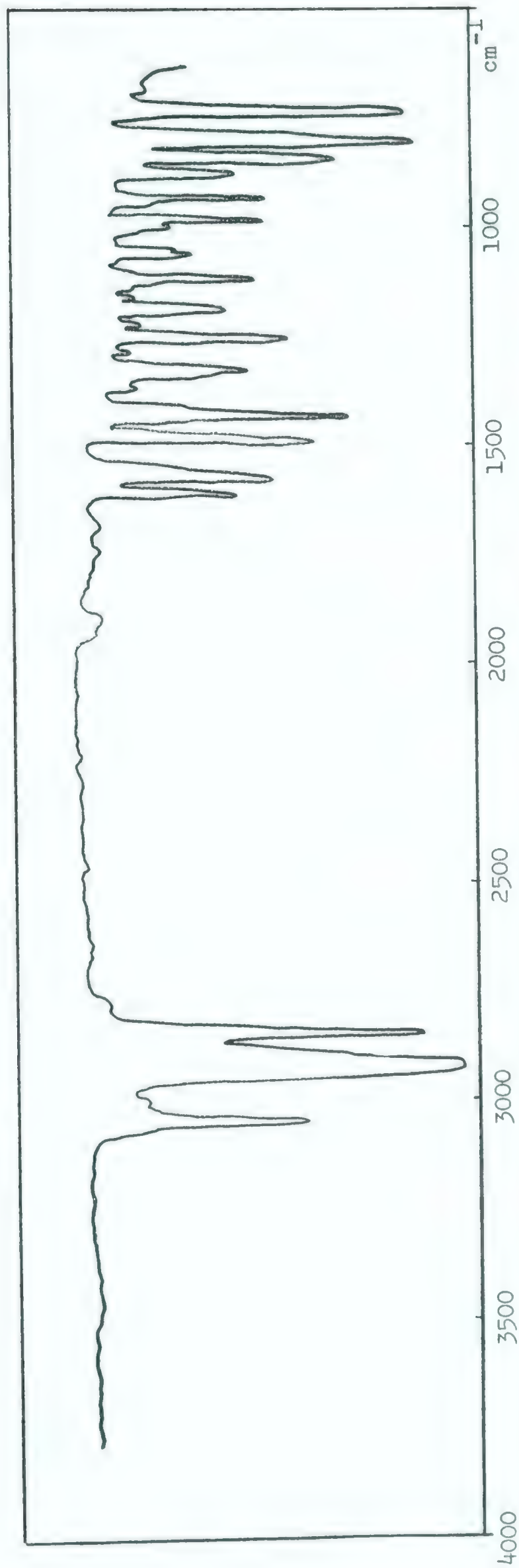


Fig. 8. Infrared absorption spectrum of cyclohexyl 2-naphthyl sulphide.
Liquid film; Perkin Elmer 221.

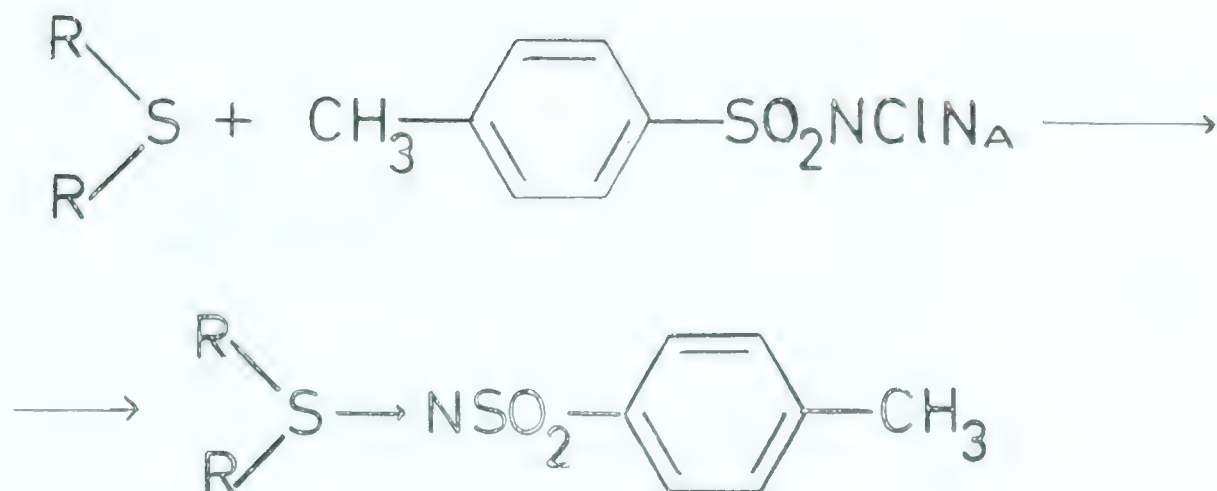
Although a steam distillation that was carried out with the oily decomposition product gave a reasonably good separation of the 2-iodobiphenyl and the sulphide the method was abandoned because it was time consuming. It was found that a vacuum distillation gave better results.

2-Iodobiphenyl and cyclohexyl 2-naphthyl sulphide were isolated from the oil in yields of 72% and 57% respectively. The sulphide has not been reported in the literature. The preparation of cyclohexyl 1-naphthyl sulphide has been described, however (51).

The sulphide isolated in the present experiment was identified by infrared spectrum, which is reproduced in Fig. 8 , analysis, and its sulphone and sulphilimine.

The spectrum shows absorption bands that can be assigned to aromatic C-H stretching vibrations (3050 cm^{-1}), aliphatic C-H stretching vibrations of the methylene group (2925 and 2847 cm^{-1}), and the stretching vibrations of the naphthalene skeleton (1616 , 1580 , and 1491 cm^{-1}). The C-H deformation vibrations of 2-substituted naphthalene cause a number of absorption bands at 880 , 845 , 804 , and 735 cm^{-1} . The pattern of these bands as observed in the spectra of several 2-naphthyl compounds that were prepared in the present work is more characteristic than their exact location, although variations are never great. Very recently Oswald and co-workers (52) reported absorptions at 893 , 855 , 813 , and 741 cm^{-1} in the infrared spectra of compounds containing the 2-naphthylthio grouping.

The sulphilimine of cyclohexyl 2-naphthyl sulphide was prepared according to the directions of McCall et al. from the sulphide and chloramin T (53).



The first sulphilimines were reported forty years ago by Mann and Pope (54). They thought that a double bond existed between the sulphur and nitrogen atoms but a few years later a sulphilimine in which the R groups were unequal was resolved (55). This was strong support for a semipolar bond between sulphur and nitrogen, and this has become the accepted bond structure.

In the last decade the sulphilimines have been gaining importance as crystalline derivatives of sulphides. The latter may be recovered from the derivatives by hydrogenolysis with hydrogen and palladium - charcoal catalyst (53).

Because very few spectra of sulphilimines have been reported in the literature the infrared spectrum of the sulphilimine prepared from cyclohexyl 2-naphthyl sulphide is reproduced in Fig. 9 .

It shows the pattern of absorption bands at 893, 861, 826, and 753 cm^{-1} , which indicate the presence of the 2-naphthyl group, and has absorption bands at 2945 and 2855 cm^{-1} caused by aliphatic C-H stretching vibrations. The region between 1320 and 900 cm^{-1} has the same pattern of peaks (and at almost the same frequencies) as in the spectrum of n-propyl phenyl sulphilimine (56) and diphenyl sulphilimine, which was prepared for purposes of comparison.

The strong split band with main absorption frequencies at 1292 and

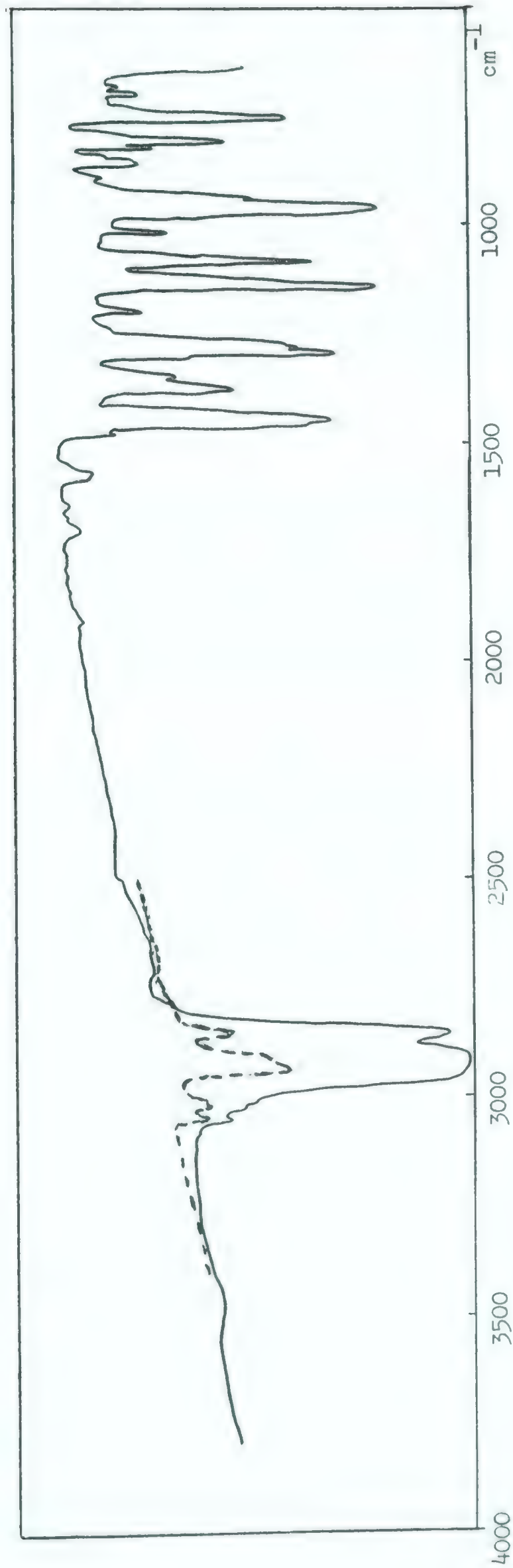


Fig. 9. Infrared absorption spectrum of cyclohexyl 2-naphthyl sulphilimine.

Mineral-oil mull (nujol) ———.

Halocarbon-oil mull - - - - -.

Perkin Elmer 221.

1279 cm^{-1} , and the sharp peak at 1140 cm^{-1} may be assigned to the SO_2^- group (42e).

All spectra of sulphilimines that are known to the present author show a strong band, which is sometimes the strongest in the spectrum, at approximately 957 cm^{-1} . This may be a characteristic absorption of sulphilimines but more evidence would be needed to arrive at a definite conclusion. The infrared spectrum of chloramin T shows a similar band at 920 cm^{-1} .

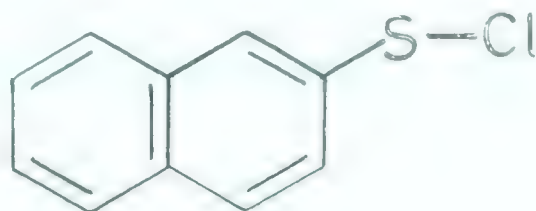
After a suspension of dibenziodolium p-toluenesulphonate in cyclohexane had been heated to reflux for some time or had been shaken for a long time at room temperature exposed to ultraviolet light, no decomposition of the salt could be detected.

B. Decomposition in carbon tetrachloride

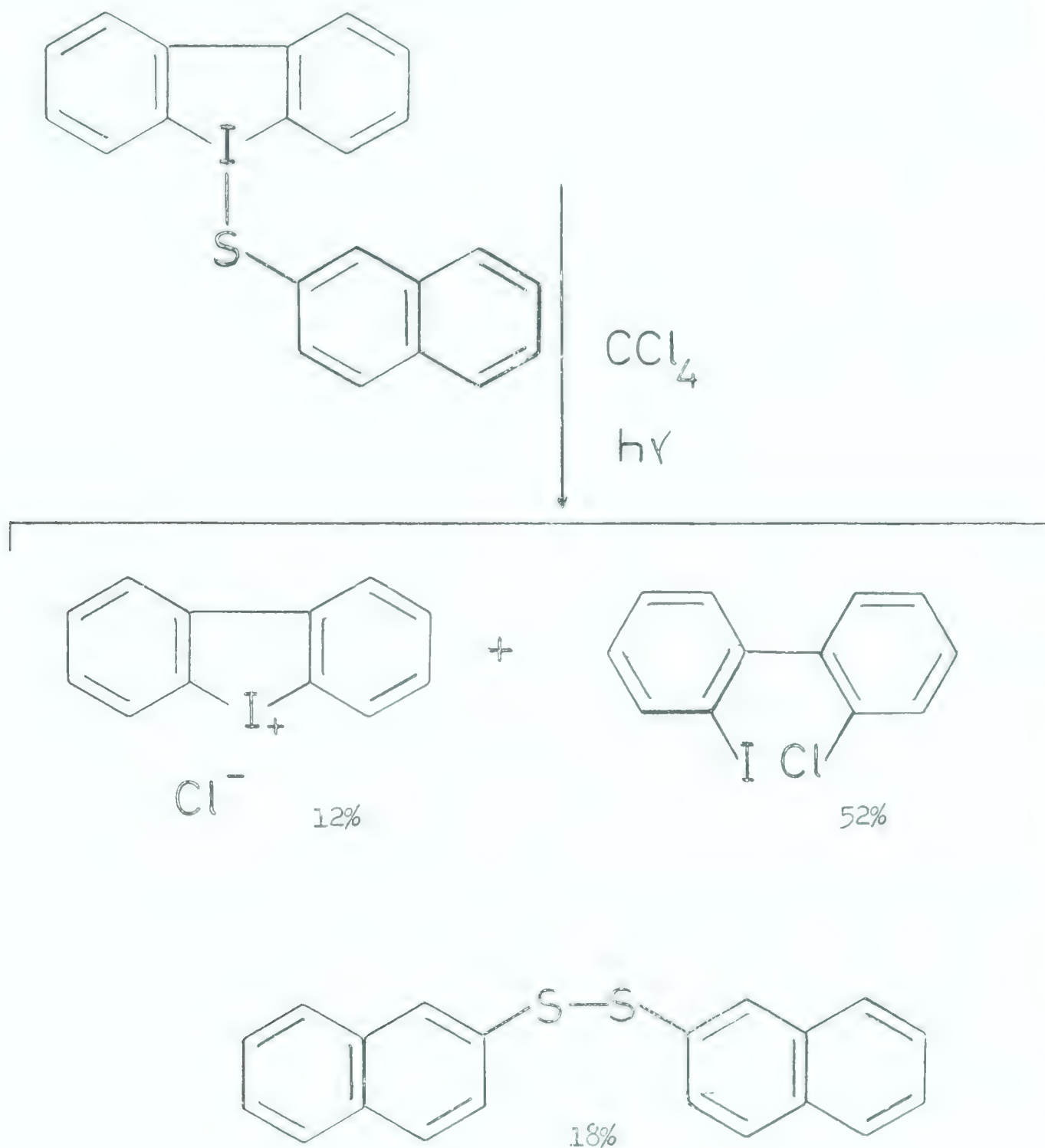
When a suspension of dibenziodolium 2-naphthalenethiolate in carbon tetrachloride was shaken in ultraviolet light, decomposition occurred. Only three pure compounds could be isolated from the reaction mixture. They were identified as dibenziodolium chloride (12%), 2,2'-dinaphthyl disulphide (18%), and 2-chloro-2'-iodobiphenyl (52%).

The disubstituted biphenyl was isolated by chromatography on alumina from a brown oil that had an odour very similar to that of hydrogen chloride. The acidic nature of the vapours could be demonstrated with litmus paper. The odour was most noticeable immediately after the vial was opened in which the oil had been stored in a nitrogen atmosphere.

On the basis of the products that had been isolated already, the presence of 2-naphthalenesulphenyl



chloride in the cell seemed plausible.

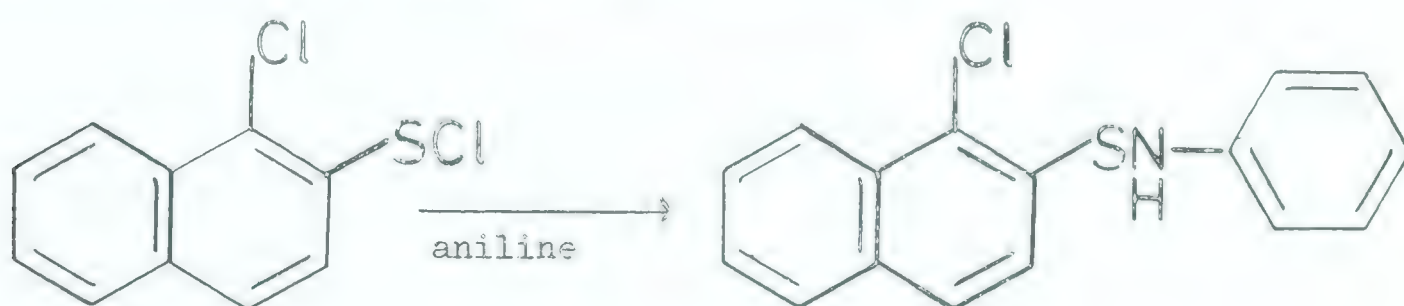


A search in the literature revealed that 2-naphthalenesulphenyl chloride is notoriously unstable among the aromatic representatives of this class of acid chlorides (57a).

The halogen atom in sulphenyl halides is reactive and the majority of reactions involving sulphenyl halides proceeds rapidly even at room temperature. When these acid halides are heated disulphides are generally formed (58).

Zincke and Eismayer (59) treated 2-naphthalenethiol with chlorine and isolated a very unstable reddish powder which could not be purified beyond the stage where it had a melting point of 50-60°. It decomposed rapidly in dry air into several products. Of these products only 2,2'-dinaphthyl disulphide was identified. When the red powder was stored in dry air there was evolution of chlorine and hydrogen chloride.

It is interesting that 1-chloro-2-naphthalenesulphenyl chloride, which can be prepared by the same reaction is far more stable (60) and can be used to prepare the corresponding sulphenanilide.



Attempts to prepare an amide from 2-naphthalenesulphenyl chloride failed (59). This sulphenyl chloride also reacted rapidly with ethanol, acetone, β -naphthol, and aniline giving in each case 2,2'-dinaphthyl disulphide. Hydrolysis of sulphenyl chlorides in general gives disproportionation with many possible products (57b).

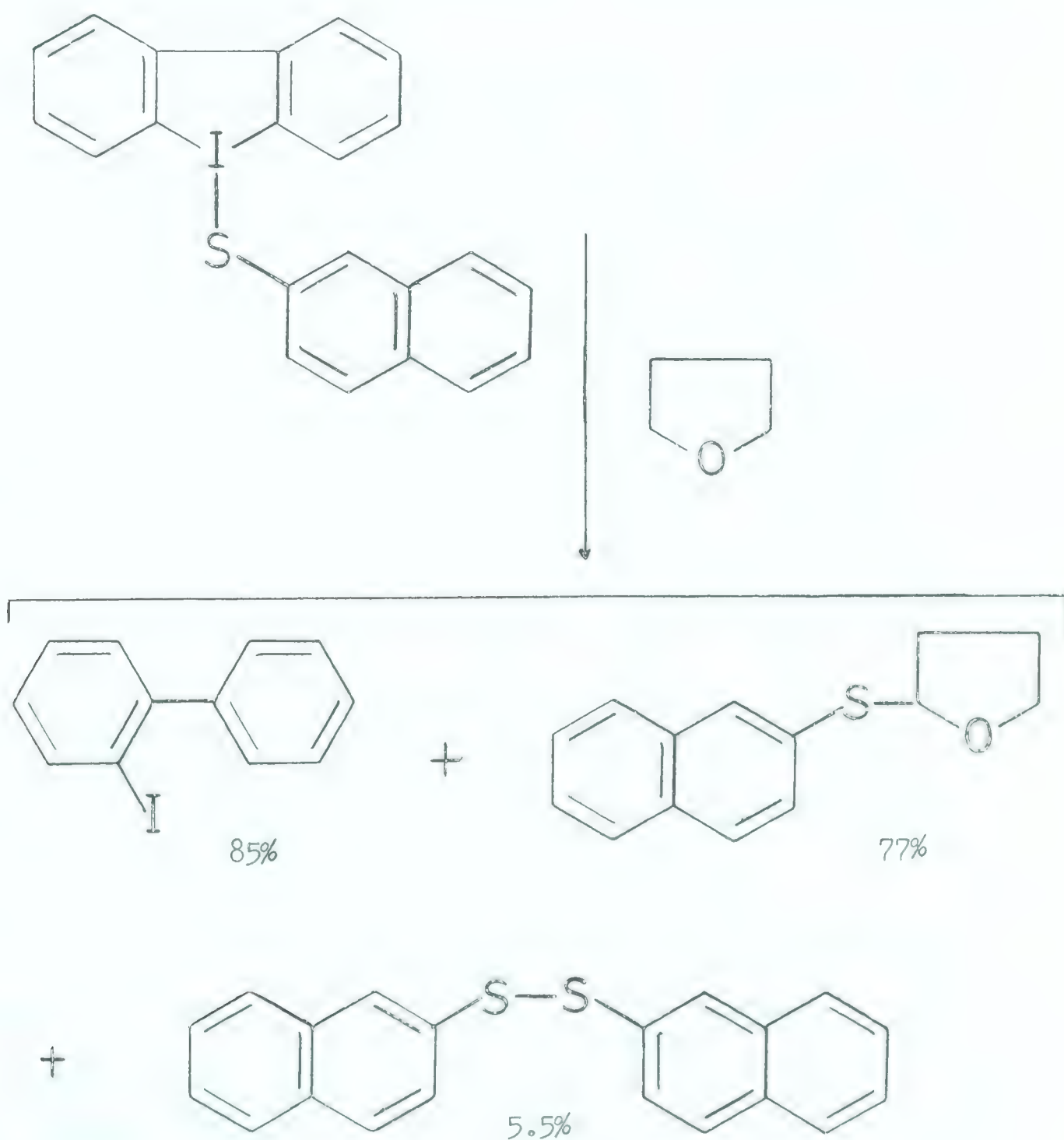
In the present work 2,2'-dinaphthyl disulphide could always be isolated from the brown oily residue after it had been standing in a closed container for some time. The same disulphide was obtained in much larger quantities when an attempt was made to prepare an anilide.

Because the disulphide was isolated after ethanol had been added to the mixture of decomposition products, the formation of the disulphide during the irradiation has not been proven.

When a suspension of dibenziodolium p-toluenesulphonate was shaken in carbon tetrachloride in ultraviolet light no decomposition of the salt occurred and no dibenziodolium chloride was formed.

C. Decomposition in tetrahydrofuran

The decomposition of dibenziodolium 2-naphthalenethiolate in peroxide-free tetrahydrofuran in a nitrogen atmosphere was rapid, especially when carried out in the sunlight.

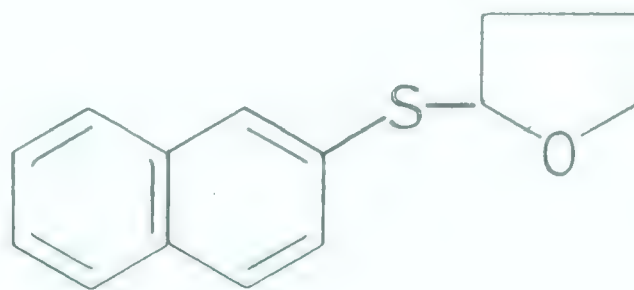


After evaporation of the solvent an oily residue was obtained from which 2,2'-dinaphthyl disulphide and 2-iodobiphenyl were isolated in yields of respectively 5.5 and 85%, and a compound for which the present author tentatively suggests the structure of 2-naphthyl tetrahydro-2-furyl sulphide in a yield of 77%.

The last two compounds could not be successfully separated by fractional distillation in vacuo because the sulphide decomposed and 2,2'-dinaphthyl disulphide was formed. Separation was achieved either by steam distillation and chromatography on alumina or by repeated chromatography alone.

The structure that is proposed for the unknown compound is supported by an analysis and the infrared spectrum which is reproduced in Fig. 10. It shows the absorptions caused by the C-H deformation vibrations of 2-substituted naphthalene (897, 852, 813, and 744 cm^{-1}) and the skeletal vibrations of naphthalene (1622, 1586, and 1498 cm^{-1}). The intense absorption band at 1050 cm^{-1} can be ascribed to the C-O-C stretching vibrations of the tetrahydrofuran ring (42f). Tetrahydrofuran itself absorbs strongly at 1076 cm^{-1} . Absorption bands at 2975, 2947, and 2870 cm^{-1} may be assigned to the aliphatic C-H stretching vibrations.

This compound was not stable and it decomposed on standing at room temperature in a closed container. One of the products was 2,2'-dinaphthyl disulphide. If the structure that is proposed for this compound is correct, it would be a partly cyclic monothioacetal. Not many monothioacetals seem to be known.



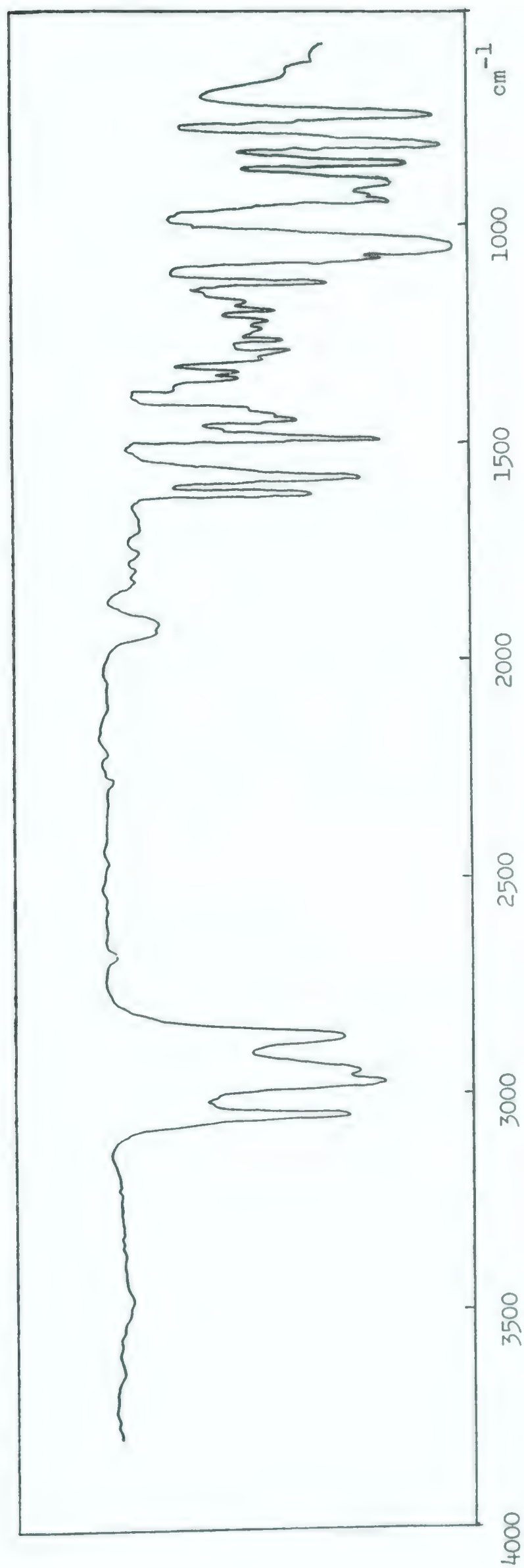


Fig. 10. Infrared absorption spectrum of 2-naphthyl tetrahydro-2(?)-furyl sulphide.

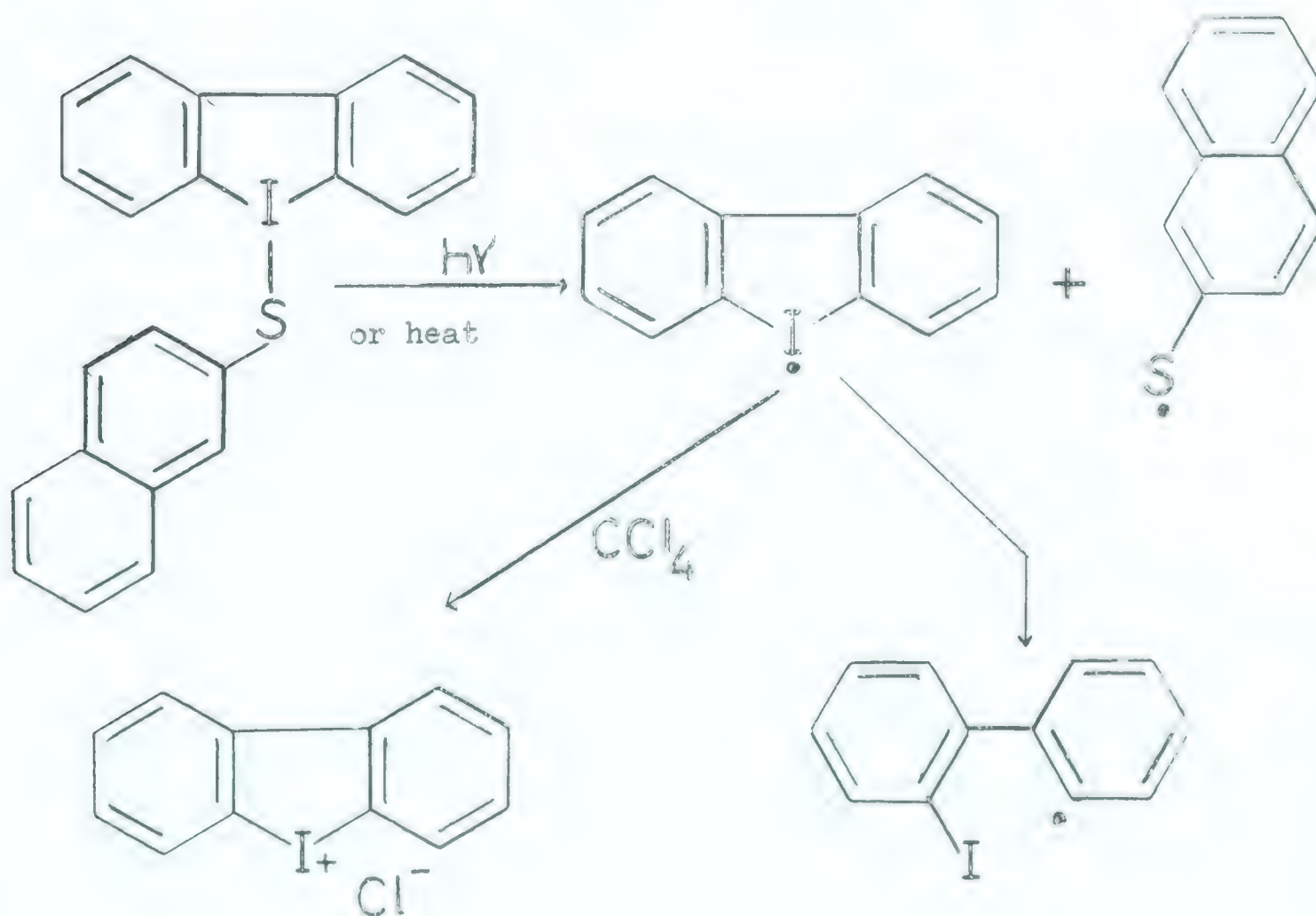
Liquid film; Perkin Elmer 221.

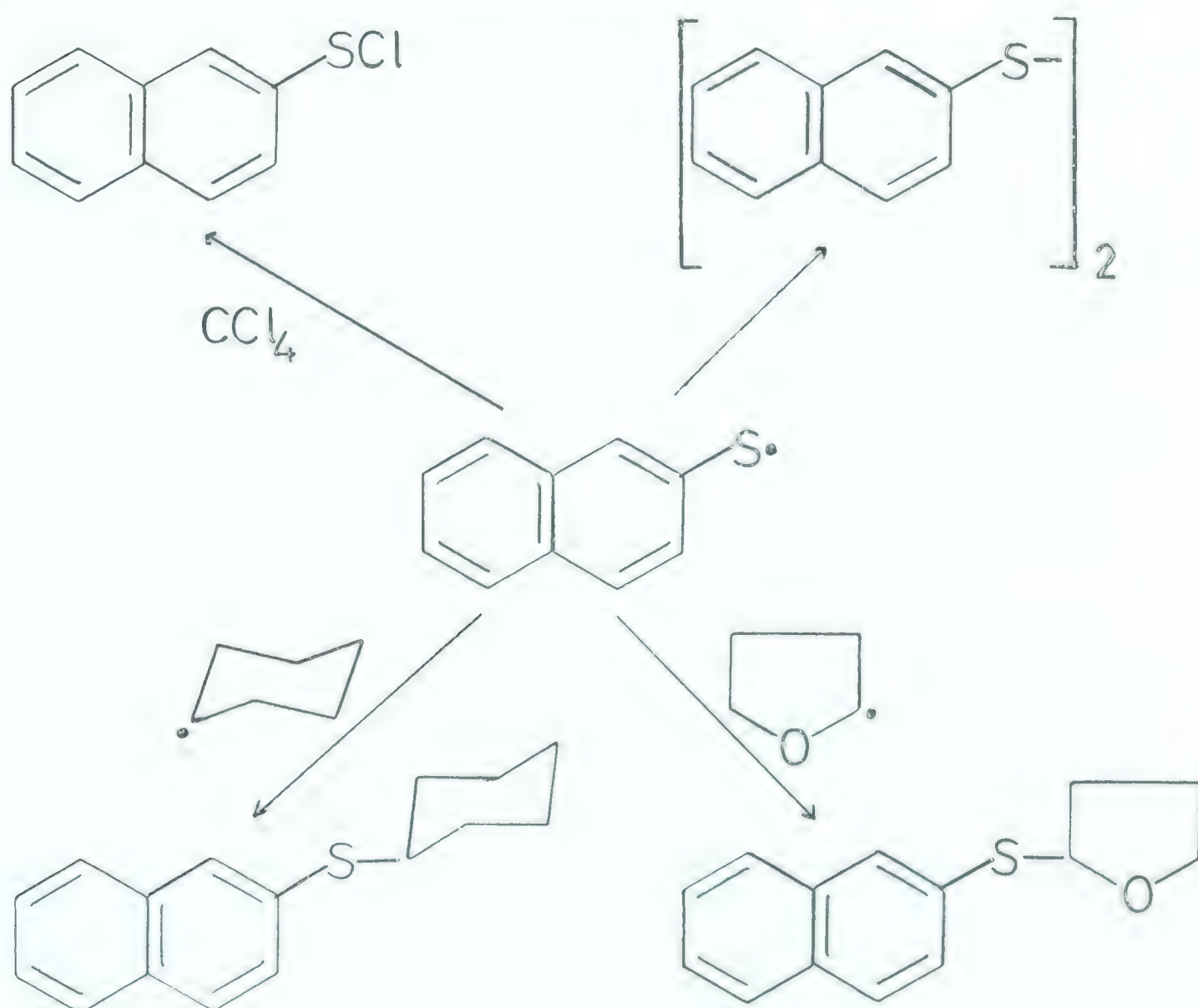
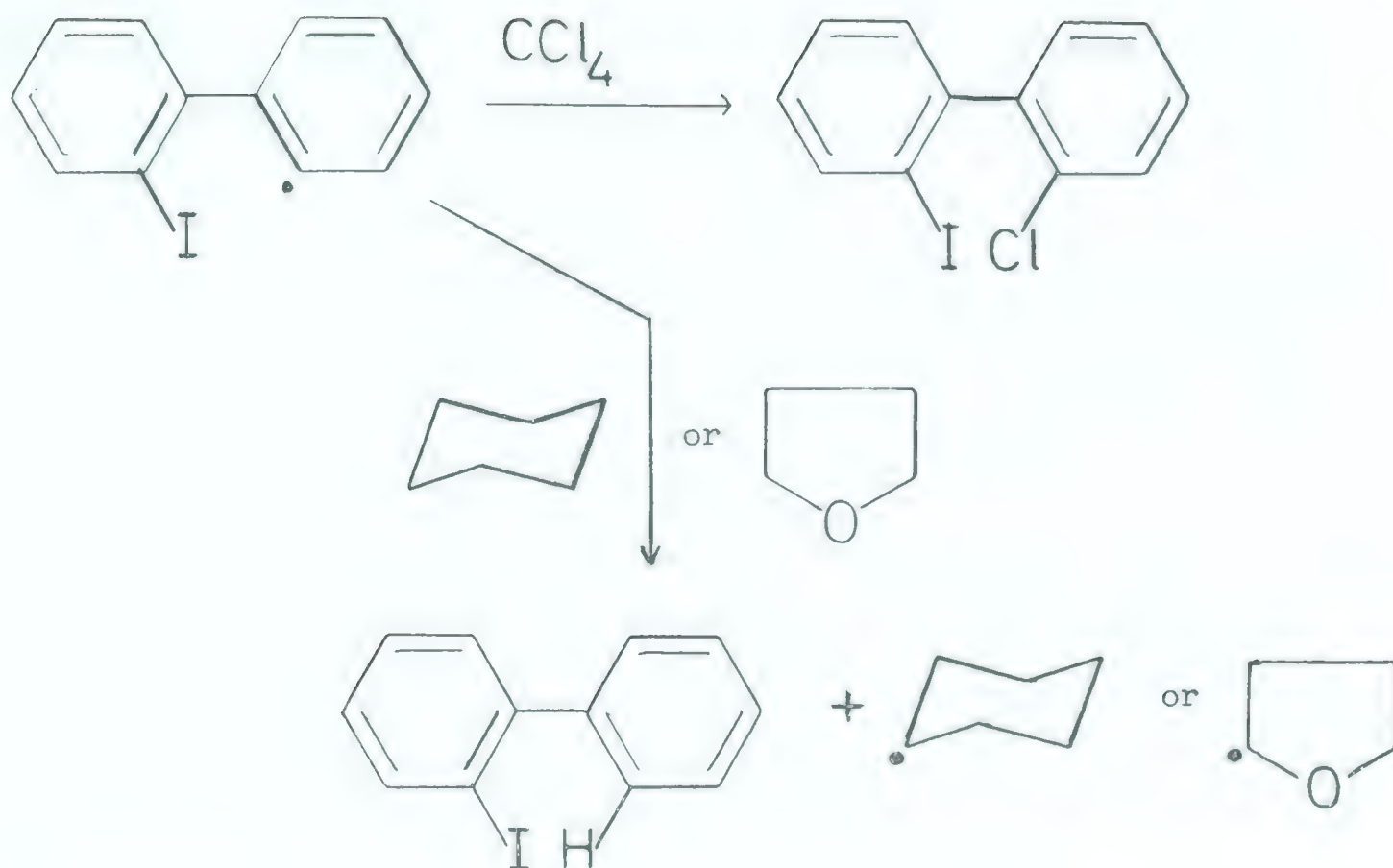
They have been prepared by addition of a thiol to a vinyl ether (61) in the presence of hydrogen chloride:



D. Discussion

Whether the decomposition takes place at room temperature in tetrahydrofuran, at reflux temperature in cyclohexane or by irradiation with ultraviolet light in carbon tetrachloride, the formation of the decomposition products of dibenziodolium 2-naphthalenethiolate may be rationalized by the assumption that the iodine - sulphur bond of a covalent thiolate breaks, giving rise to two radicals, each of which may react further.





Other reactions are almost certainly taking place and not all products have been isolated and identified. However, the formation of those that have been identified can not be rationalized without the use of a radical mechanism.

At first sight it might be argued that the radicals which initiate the reaction are formed by irradiation of the solvent or by some other process, for instance:



If the thiolate is an ionic compound it seems hard to conceive an attack by the radical on the ions, with, for instance, the formation of dibenziodolium chloride.

When a suspension of dibenziodolium p-toluenesulphonate in carbon tetrachloride was shaken for more than seven days in ultraviolet light no decomposition occurred and no chloride ion could be detected in the recovered dibenziodolium salt.

Irving and Reid (62) who studied the photodecomposition of dibenziodolium halides and some other iodonium salts found that dibenziodolium iodide decomposed when it was irradiated in chloroform, but the decomposition of the other halides was barely detectable. They did not study the products but suggested a covalent iodide as an intermediate before decomposition into radicals.

The present author considers the results obtained in the decomposition of dibenziodolium 2-naphthalenethiolate in various solvents as additional evidence for the covalent character of the iodine - sulphur bond in this compound.

SECTION 3

EXPERIMENTAL

Part I

Some Important Starting Materials

2,2'-Dinitrobiphenyl

The procedure of Fuson and Cleveland (63) was used for the preparation of 2,2'-dinitrobiphenyl from 1-chloro-2-nitrobenzene.

2,2'-Diaminobiphenyl

In a small-scale experiment it was found that the hydrogenation of 2,2'-dinitrobiphenyl could very easily be effected at low pressure with platinum as a catalyst in a Parr apparatus. The yield of the reaction was excellent.

Portions (20 g.) of the dinitro compound were dissolved in 200 ml. of ethyl acetate, 300 mg. of platinum dioxide was added and hydrogenation was started at an initial pressure of 3 atm. The pressure was several times adjusted to 3 atm. during the course of the reaction. The calculated volume of hydrogen reacted in general in about two hours. After filtration of the reaction mixture it was extracted with dilute hydrochloric acid. The extract was added slowly to a dilute solution of sodium hydroxide (excess), which was kept at approximately 10°, under vigorous stirring. The diamino compound was obtained as a yellow precipitate that contained a considerable quantity of water. Dilute solutions were used

and the temperature was controlled to prevent the diamino compound from separating as an oil. When the alkaline solution was added to the acid solution an oil was always formed first, even at 10°.

The yield of crude 2,2'-diaminobiphenyl was 129 g. from 182.5 g. of 2,2'-dinitrobiphenyl; that is 93.5% of the theoretical yield. A small sample after crystallization from ethanol had m.p. 78.5-79.5°. The reported m.p. is 79-80° (64).

The catalytic reduction of 2,2'-dinitrobiphenyl in ethanol in the presence of Raney nickel to benzo[c]cinnoline has been reported (62).

2-Bromo-2'-aminobiphenyl (as the hydrochloride)

2,2'-Diaminobiphenyl was acetylated by Sako's method (64) and the yield of 2-amino-2'-acetamidobiphenyl was 80%. The m.p. was 92-96°, slightly higher than the reported m.p. 89-90° (64).

This compound was diazotized in 40% hydrobromic acid. After addition of a solution of cuprous bromide in hydrobromic acid the temperature of the cold mixture was allowed to rise slowly to room temperature. A rapid rise in temperature resulted in a lower yield.

The tar that was formed was dissolved in a mixture of ethanol and hydrochloric acid. This solution was refluxed for one hour, made alkaline and subjected to a steam distillation. The product was isolated as the hydrochloride, which after one crystallization from water had m.p. 176-182°. The reported m.p. is 184-185° (28). The compound was not purified further. The overall yield of diazotization and hydrolysis was 35% when starting with 50 mmoles of acetamido compound.

Dibenzobromolium salts

The preparation of dibenzobromolium chloride and iodide from

2-bromo-2'-aminobiphenyl has been reported by Sandin and Hay (28).

Their method was used.

2-Iodobiphenyl

Dilute sulphuric acid instead of dilute hydrochloric acid was used as solvent (65) in the diazotization of 2-aminobiphenyl, which was carried out as described by Gilman and co-workers (66). The yield of 2-iodobiphenyl was always about 80%.

Dibenziodolium salts

The bisulphate and sulphate were prepared from 2-iodobiphenyl by oxidation with peracetic acid and cyclization with concentrated sulphuric acid (67). Other less soluble salts, for instance the chloride and iodide, were prepared by metathesis.

Dibenziodolium p-toluenesulphonate crystallized in the form of needles when p-toluenesulphonic acid was added to a hot solution of the sulphate in water. Its m.p. was 297-298°.

Analysis:

Calculated for $C_{19}H_{15}O_3SI$: S, 7.12 ; I, 28.18.

Found : S, 7.13 ; I, 28.42.

Phenyliodoso dichloride

Iodobenzene was treated with chlorine in cold chloroform (cooling with ice) according to the method of Lucas and Kennedy (68a). The yield of iodoso dichloride was almost quantitative.

Diphenyliodonium chloride

Iodosobenzene was prepared from phenyliodoso dichloride (68b).

The preparation of diphenyliodonium chloride from iodosobenzene was carried out as described by Beringer and co-workers (9). To obtain the highest possible yield the diphenyliodonium cation was precipitated as the very insoluble iodide that was converted into the chloride by the method of Forster and Schaeppi (69).

Phenyllithium

a. From bromobenzene and lithium.

The procedure described by Gilman and Morton (70) was always used. Small pieces of broken glass were added to the stirred mixture to increase the surface of exposed clean lithium. The yield was determined by hydrolysis of a small aliquot and titration with standard acid, using phenolphthalein as indicator.

b. From diphenylmercury and lithium (71).

In a typical preparation 4 g. of diphenylmercury (Eastman Kodak Co., White Label) was stirred in 20 ml. of dry ether with 0.6 g. of lithium shavings for 6 hours. The solution was filtered through a glass filter. The yield determined by titration was 80%.

p-Methoxyphenyllithium and p-dimethylaminophenyllithium

The method reported in the literature was used (72). When titrating a hydrolyzed aliquot of p-dimethylaminophenyllithium it was sometimes hard to determine the end point, but with phenolphthalein as indicator it was usually possible (73).

2,2'-Diiodobiphenyl

Thermal decomposition of 11.5 g. of dibenziiodolium iodide at 230° in a round-bottomed flask produced a dark oily tar. Before this tar had

solidified ethanol was added and the hot orange-brown alcoholic solution was decolourized partly with charcoal. After cooling colourless crystals were isolated. The yield of crude 2,2'-diiodobiphenyl was 8.3 g., or 72% of the theoretical yield. The m.p. of the product was 105-108°; the pure compound melts at 110° (7). No further purification was attempted and the compound was used for the preparation of 2,2'-dilithiobiphenyl.

2-Chloro-2'-iodobiphenyl

An attempt to prepare 2-chloro-2'-iodobiphenyl by thermal decomposition of dibenziiodolium chloride was a failure. This was not unexpected in view of results obtained earlier by other workers (74). Therefore another method was used to obtain this compound.

A solution of 22.6 g. of 2-amino-2'-acetamidobiphenyl (100 mmoles) in a mixture of 120 ml. of concentrated hydrochloric acid and 50 ml. of water was cooled to 0°. A solution of 7.0 g. of sodium nitrite (100 mmoles) in 10 ml. of water was slowly added between 0 and 5°. A solution of 8 g. of cuprous chloride in 10 ml. of concentrated hydrochloric acid was added and the temperature was allowed to rise slowly to room temperature. The dark tar that was formed was hydrolysed in a mixture of ethanol and hydrochloric acid and 14.0 g. of the crude hydrochloride of 2-chloro-2'-aminobiphenyl was obtained. This method of preparation has been used by other workers (28).

The product was diazotized again in 10% hydrochloric acid between -5 and 2°. The solution of diazonium salt was added to a cold solution of excess potassium iodide in water, which had a temperature of -3°. When the temperature of the mixture rose slowly the decomposition of the diazonium salt became violent as a result of many small explosions in the dark brown tar that was formed. After the reaction mixture had been ex-

tracted with ether the extract was washed with a concentrated solution of sodium thiosulphate. A solidifying red-brown oil was isolated. After repeated decolourizations and recrystallizations (7 times) in ethanol 3.8 g. of colourless 2-chloro-2'-iodobiphenyl (12 mmoles) was obtained with m.p. 62-63.5°. The reported m.p. is 63-64° (75). The overall yield on the basis of the acetamido compound was 12%.

SECTION 3

EXPERIMENTAL

Part II

Attempts to Prepare Derivatives of the Unknown

Compound Iodole and its Bromine Analogue

Reactions between dibenziodolium halide and aromatic organolithium compounds

Clauss (3) allowed dibenziodolium iodide to react with a solution of phenyllithium in dry ether and obtained 5-phenyldibenziodole. Except for the fact that the reaction and all subsequent manipulations had to be carried out in a nitrogen atmosphere the preparation as described by the author was simple. The present author found that the following procedure gave the most satisfactory results.

To 3-6 g. of dibenziodolium halide in a 100-ml. round-bottomed glass-stoppered flask was added 5 ml. of dry ether. The flask was thoroughly flushed with dry nitrogen. Addition of the solution of organolithium compound, which was usually 1 M, was carried out in a nitrogen atmosphere. A so-called dry-box filled with nitrogen was used for this purpose and for most of the following manipulations. An ethereal solution of the lithium compound containing 20-25% excess of the organometallic compound was added; the flask was tightly stoppered and vigorously shaken for 2 hours. Upon mixing there was a slight heat effect and the solution turned yellow. After shaking had been stopped a bright yellow precipitate settled and a colourless finely divided material, probably lithium halide,

was visible. Unless the yellow compound was needed immediately for further investigation it was better not to open the flask but store it at 3-4° till needed.

To isolate the yellow material the contents of the flask was filtered in a nitrogen atmosphere; the precipitate was washed on the filter three times with dry ether to remove any excess organolithium compound and then three times with distilled water to dissolve lithium salt. The isolated compounds had generally a bright yellow colour. They were transferred to a nitrogen-filled vial and stored at 3-4°. Even at that temperature decomposition often started soon. It was found that once a vial had been opened for a few seconds to take a sample of the compound decomposition was very rapid.

Using the outlined procedure the reaction between dibenziodolium chloride and phenyllithium, p-methoxyphenyllithium and p-dimethylaminophenyllithium was carried out.

Solutions of phenyllithium were prepared from bromobenzene or diphenylmercury and lithium. Solutions prepared either way gave the same results in the final reaction, it seemed.

The yellow compound prepared from phenyllithium and dibenziodolium halide decomposed between 95 and 115°. Clauss (3) reported for recrystallized 5-phenyldibenziodole decomposition between 105 and 115°. All attempts by the present author to recrystallize the product from tetrahydrofuran were unsuccessful because rapid decomposition occurred. The tetrahydrofuran had been treated with cuprous chloride to remove peroxide (76). It had been distilled again and when no peroxide was found in a test it was used immediately.

Other solvents for a recrystallization were tried but none was found suitable. The solubility in methanol and ethanol was very low.

In chloroform or carbon tetrachloride 5-phenyldibenziodole decomposed rapidly at room temperature and solutions in benzene and toluene started to darken immediately.

The products from the reaction between p-methoxyphenyllithium or p-dimethylaminophenyllithium and dibenziodolium chloride were very unstable. The product that was presumed to be 5-(p-methoxyphenyl)dibenziodole decomposed to a dark brown tar in one hour after the vial in which it was kept under nitrogen had been opened for a few seconds.

Reaction between 2,2'-dilithiobiphenyl and phenyliodoso dichloride

The preparation of 2,2'-dilithiobiphenyl was carried out as reported by Wittig and Herwig (77) with a prolonged reflux period as recommended by Wittig and Lehmann (78).

To a solution of 3.0 g. of 2,2'-diiodobiphenyl (7.2 mmoles) in 48 ml. of dry ether was added 0.6 g. of lithium shavings (86 mg.atoms). The ether started to reflux and after 30 minutes a solution of 3.0 g. of the diiodo compound (7.2 mmoles) in 30 ml. of ether was added dropwise. Reflux was continued for 90 minutes after addition of the diiodocompound. After filtration of the solution through a glass filter the yield was determined by titration of a hydrolyzed aliquot (90%).

To a stirred suspension of 1.37 g. of phenyliodoso dichloride (5 mmoles) in 10 ml. of dry ether was slowly added 30 ml. of a 0.2 M solution of 2,2'-dilithiobiphenyl in ether. The reaction was carried out at 0° in a nitrogen atmosphere. After addition of this solution the colour of the mixture was orange brown. The lithium compound had nearly all reacted because the mixture was found to be 0.06 M in organometallic. Water was added and the layers were separated. The ethereal solution was dried with anhydrous sodium sulphate and the solvent was evaporated

in vacuo. The residue was a brown oil with the odour of iodobenzene. No 5-phenyldibenziodole was isolated.

Attempt to prepare pentaphenyliodole

Diphenylacetylene was prepared from trans-stilbene in an overall yield of 64% (79).

A solution (suspension) of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene in ether was prepared by the method of Braye and co-workers (37) : To a solution of 5.0 g. of diphenylacetylene (28 mmoles) in 15 ml. of dry ether was added 0.59 g. of lithium shavings (85 mg.atoms). The mixture was shaken for 150 minutes in a nitrogen atmosphere and it turned rapidly intensely red. After 25 ml. of dry ether had been added the red suspension was separated from excess lithium using a large syringe. It was transferred to a flask filled with nitrogen and cooled to -10° .

Phenyliodoso dichloride (4.0 g., 14.5 mmoles) was added in small portions. Every addition caused local boiling of the ether. The reddish brown colour of the suspension disappeared gradually. After the reaction mixture had reached room temperature a suspension of colourless material in a yellow ethereal solution was obtained. When water was added the colourless product dissolved immediately and probably this was lithium chloride. No pure compounds were isolated from the ethereal solution. The experiment was not repeated.

Reaction between dibenzobromolium chloride and phenyllithium

In a few preliminary experiments it was found that an ethereal solution of phenyllithium when added to a suspension of dibenzobromolium chloride in dry ether in a nitrogen atmosphere at room temperature gave a violent reaction without formation of a solid.

When the suspension of bromolium compound was cooled in a dry ice - acetone mixture at -75° no reaction seemed to occur when the lithium compound was added. In other tests it was found that at -15° and -30° the reaction was still immediate and vigorous, that between -30° and -45° the reaction was appreciably slower and that a yellow colour was noticeable which faded rapidly, and that below -50° no reaction seemed to occur. All these tests were carried out on a very small scale.

The final experiment was carried out on a larger scale. A suspension of 0.72 g. of dibenzobromolium chloride (2 mmole) in 5 ml. of dry ether was cooled to -60° in a small round-bottomed flask, which was filled with nitrogen. A 0.9 M solution of phenyllithium in ether was cooled to -80° and 3.3 ml. of it (3 mmoles) was added to the suspension. The reaction mixture turned yellow but the colour faded and after 10 minutes had disappeared. Stirring was continued for 2 hours at -75° and the reaction mixture was stored overnight at -80° . When a small quantity of the grey solid material was removed from the reaction flask on a pre-cooled spatula and held exposed to air at room temperature part of the powder decomposed with small explosions. This product was not investigated further. Very unstable compounds had been formed apparently.

SECTION 3

E X P E R I M E N T A L

P a r t III

Decomposition of Dibenziodolium Salts
in Alcoholic Solutions

Reactions in methanol in the presence of dimedone

a. To a solution of 1.15 g. of sodium (50 mg.atoms) in 125 ml. of reagent-grade methanol was added 4.90 g. of dimedone (35 mmoles) and 10.15 g. of dibenziodolium iodide (25 mmoles). During the following reflux period most of the iodide dissolved and the solution turned orange. The reaction was carried out in a nitrogen atmosphere.

After 40 hours of reflux the mixture was filtered. The undissolved material was washed with some methanol and then dried. The recovered dibenziodolium iodide weighed 2.2 g. (5.4 mmoles). When the orange filtrate was cooled in a dry ice - acetone bath a crystalline precipitate was formed that was recrystallized from 95% methanol. This way 1.52 g. of 2,2'-methylene-bis(5,5-dimethyl-1,3-cyclohexanedione) was obtained (5.2 mmoles), with m.p. 191-194°. The reported m.p. is 190-192° (8). The infrared spectrum of this compound was identical with that of an authentic sample with m.p.190-193°, which was prepared from formaldehyde and dimedone (41b). Admixture did not depress the m.p.

The yield of formaldehyde derivative was 26.5% based on the assumption that one molecule of aldehyde originated from the decomposition of one dibenziodolium cation.

b. To a solution of 2.30 g. of sodium (100 mg.atoms) in 250 ml. reagent-grade methanol was added 9.80 g. of dimedone (70 mmoles) and 16.35 g. of dibenziodolium sulphate (25 mmoles). The stirred reaction mixture was heated to reflux for 24 hours and kept at room temperature for 16 hours in a nitrogen atmosphere.

All the dibenziodolium sulphate had gone into solution and sodium sulphate was removed from the reaction mixture by filtration. The filtrate was concentrated to a quarter of its original volume and cooled in a dry ice - acetone mixture. An oil, which contained solid material, could be separated from the methanolic solution A.

The oily material was redissolved in boiling methanol, the solution concentrated and cooled in dry ice - acetone. Again an oil, but also some crystalline material, was formed. Part of these crystals were separated mechanically from the oil and recrystallized from methanol giving 0.8 g. of 2,2'-diiodobiphenyl, which was identified by its infrared spectrum and showed no depression of its m.p. when mixed with an authentic sample of 2,2'-diiodobiphenyl (for preparation see Part I of this section).

The rest of the oily material was subjected to a steam distillation and 1.6 g. of 2-iodobiphenyl, identified by comparison of its infrared spectrum with that of authentic material, was isolated from the distillate. In addition a small quantity of solid was isolated, which was purified by sublimation. This proved to be more 2,2'-diiodobiphenyl (40 mg.), identified as before.

Water was added to the methanolic solution A. An oil was formed and the mixture was extracted with ether. This way an extracted aqueous solution B and an ethereal extract were obtained.

The ethereal extract: The ether was evaporated. Petroleum ether

(Skellysolve) was added to the oily residue and dissolved most of it. The insoluble material was twice recrystallized from ethanol giving 0.15 g. of 2,2'-methylene-bis(5,5-dimethyl-1,3-cyclohexanedione), which was identified as before.

From the solution in petroleum ether 3.6 g. of 2-iodobiphenyl was isolated after evaporation of the solvent and steam distillation of the residue. It was identified by its infrared spectrum.

The aqueous solution B: After concentration the pH was adjusted to 8-9. The precipitate that was formed was recrystallized from 95% methanol giving 3.7 g. of 2,2'-methylene-bis(5,5-dimethyl-1,3-cyclohexanedione). The only other material isolated from solution B was a brown glasslike mass, weighing 2.9 g., which could not be identified.

In total 0.84 g. of 2,2'-diiodobiphenyl (2 mmoles, 4%), 5.2 g. of 2-iodobiphenyl (18.5 mmoles, 37%) and 3.85 g. of 2,2'-methylene-bis(5,5-dimethyl-1,3-cyclohexanedione) (13 mmoles) were isolated. The yield of the formaldehyde derivative was 26% when it is assumed that one molecule aldehyde originates from the decomposition of one dibenziiodolium cation.

c. A solution of 2.45 g. of dimedone (17.5 mmoles) and 0.6 g. of sodium (26 mg.atoms) in 60 ml. of reagent-grade methanol was refluxed for 37 hours under nitrogen. No dimedone derivative of formaldehyde could be isolated and only dimedone was recovered.

Reactions in methanol in the absence of dimedone

a. To a boiling solution of 1.15 g. of sodium (50 mg.atoms) in 150 ml. of reagent-grade methanol was added 8.18 g. of dibenziiodolium

sulphate (12.5 mmoles) and the distillate was collected. The whole apparatus had been flushed with nitrogen before the experiment was started. While methanol was added continuously to the reaction mixture 250 ml. of distillate was collected. It gave a positive reaction with Tollens' reagent, which indicated the presence of a reducing agent. The methanol used in this experiment gave a negative reaction with Tollens' reagent.

To isolate formaldehyde in the form of its dimedone derivative the procedure for quantitative analysis of formaldehyde was used (41a): Fifty milliliters of distillate was buffered with sodium acetate - hydrochloric acid at pH 4.6 and a solution of 2.8 g. of dimedone in 125 ml. of hot water was added. The mixture was kept at 80° for 10 minutes and left overnight to cool to room temperature. After filtration 24.4 mg. of 2,2'-methylene-bis(5,5-dimethyl-1,3-cyclohexanedione) was obtained in the form of long needles. It was identified by comparison with authentic material.

b. From a solution of 1.15 g. of sodium (50 mg.atoms) in 150 ml. of reagent-grade methanol the distillate was collected under nitrogen. The distilled methanol gave no reaction with Tollens' reagent. This indicated the absence of reducing agents, including formaldehyde.

Reaction in tertiary butyl alcohol; 2-iodo-2'-t-butoxybiphenyl

To a solution of 1.84 g. of sodium (80 mg.atoms) in 120 ml. of t-butyl alcohol was added 13.08 g. of dibenziodolium sulphate (20 mmoles) and the mixture was heated to reflux for 32 hours in a nitrogen atmosphere. After cooling the reaction mixture was filtered. From the brown, viscous,

sticky, insoluble material no compounds were isolated that could be identified. The filtrate was diluted nine times with water and the solution was made acidic with hydrochloric acid (pH 2-3). Sodium chloride was added and this mixture was twice extracted with ether. After the ethereal extract had been dried with anhydrous magnesium sulphate and the solvent had been evaporated a vacuum distillation was carried out with the residue. Two fractions were collected:

fraction 1, collected between 108 and 119°, but most of it at 115-119° (0.08-0.10 mm.), weighing 4.1 g., and

fraction 2, collected at 119-127° (0.08-0.10 mm.), weighing 1.4 g.

There was a very viscous brown residue in the distillation flask weighing 2.0 g. The infrared spectra taken from material collected in fractions 1 and 2 were identical except for a very weak absorption peak in the spectrum of fraction 2, attributed to a hydroxyl group probably present as a result of slight decomposition during the final stages of the distillation. The infrared spectrum of the material collected in fraction 1 has been reproduced in Fig. 1, and is discussed in Part II of Section 2. The main product of this reaction was apparently 2-iodo-2'-t-butoxybiphenyl. When the very small quantity of hydroxylic impurity is neglected the yield of this product was 5.5 g. or 39%.

Analysis:

Calculated for $C_{16}H_{17}OI$: I, 36.08.

Found : I, 36.50.

In another experiment on the same scale, but using dibenziodolium chloride as the starting material, the yield was 31% and the product was collected at 105-127° (0.06-0.09 mm.).

Attempt to synthesize 2-iodo-2'-butoxybiphenyl

The synthesis of 2-iodo-2'-hydroxybiphenyl was carried out as reported in the literature (7). 2-Iodo-2'-acetoxybiphenyl was prepared from 20 g. of dibenziodolium sulphate. The crude acetoxy compound was not distilled before methanolysis to 2-iodo-2'-hydroxybiphenyl was carried out. The phenol was isolated as a very viscous oil, b.p. 113-118° (0.25 mm.), which after two days at room temperature solidified to a colourless material, m.p. 63-64°. The reported m.p. is 62.5-63° (7). The yield was 13.2 g. or almost 72% based on the quantity of dibenziodolium sulphate.

The alkylation of the phenol was attempted with use of the results and directions of Stevens (43):

2-Iodo-2'-hydroxybiphenyl (7.0 g., 23.6 mmoles) was added to 60 ml. of liquid isobutene at -25°. After addition of 4 μ l. of 40% sulphuric acid the mixture was stirred for 2 hours while the temperature was kept between -20° and -10°. After evaporation of the olefin the starting material was recovered unchanged.

SECTION 3

E X P E R I M E N T A L

P a r t I V

Preparation of Some New Dibenziodolium CompoundsDibenziodolium hydroxide monohydrate

A hot filtered solution of 10.0 g. of dibenziodolium sulphate (15.3 mmoles) in 650 ml. of water was added to a solution of 3.66 g. of sodium hydroxide (92 mmoles) in 50 ml. of water. When this mixture was cooled slowly to 4° fine needle-shaped crystals appeared. After filtration a solution of 20 g. of sodium hydroxide in 100 ml. of water was added to the filtrate and the mixture was cooled again to 4°. A second crop of crystals was obtained.

The crude product was recrystallized from water. The dibenziodolium hydroxide monohydrate was dried at room temperature, giving 4.38 g. of colourless needles, which formed a feltlike mass. The yield of hydroxide was only 45.4% because considerable losses occurred in the recrystallization.

Analysis:

Calculated for $C_{12}H_9OI \cdot H_2O$: H_2O , 5.73.

Found : H_2O , 5.75.

The compound turned yellowish brown when dried at 75° to constant weight.

Analysis:

Calculated for $C_{12}H_9OI$: I, 42.86.

Found : I, 42.80, 43.14.

When the m.p. of the compound was determined the colour of the sample started to darken at 110° . This was in one case followed by explosive decomposition at 115° , at other times by slowly proceeding decomposition up to 130° , 155° or 165° at which temperature the compound had melted completely.

The infrared spectrum of this compound is reproduced in Fig. 2 and is discussed in Part III of Section 2.

Dibenziodolium 5,5-dimethyl-3-keto-1-cyclohexenolate dihydrate (or dimedate dihydrate)

A solution of 8.52 g. of dimedone (60.8 mmoles) and 2.43 g. of sodium hydroxide (60.8 mmoles) in 50 ml of water was added to a filtered solution of 20.0 g. of dibenziodolium sulphate in 1800 ml. of hot water.

The mixture was yellow and when the solution was cooled slowly crystallization began. The cold solution was almost colourless and contained slightly tan crystals, which were collected and weighed 24.5 g. when dry. When the m.p. of this material was determined the colour started to darken between 125 and 140° , and rapid decomposition occurred between 155 and 160° .

The product could be recrystallized from a large volume of water after which it was almost colourless. When chloride anion was added to a solution in water dibenziodolium chloride precipitated.

It was fairly soluble in chloroform, giving a yellow solution. Solutions in methanol, ethanol, and carbon tetrachloride were also

yellow when warm, but the colour faded almost completely when the solutions were cooled. When water was added to the warm yellow solution in ethanol, the colour disappeared and could not be restored by heating the mixture again.

When a ground sample of the product was dried in vacuo (1-5 mm.) its colour changed from almost colourless to yellow in 30 minutes, becoming greenish yellow after three days. When a sample of the dry coloured material was exposed to air, it became colourless again. The compound also turned yellow when it was dried at 50-55° till constant weight was reached.

Analyses:

Calculated for $C_{20}H_{19}O_2I$: I, 30.34.

Found : I, 30.38, 30.20.

Calculated for $C_{20}H_{19}O_2I \cdot 2 H_2O$: H_2O , 7.93.

Found : H_2O , 7.50.

The analyses confirmed that the salt of the dibenziodolium cation and the anion of dimedone had been formed. The yield of 24.5 g. of dibenziodolium dimedate dihydrate was 89% of the theoretical yield.

The infrared spectrum of this compound has been reproduced in Fig. 3, and is discussed in Part III of Section 2.

Dibenziodolium barbiturate monohydrate

A solution of 3.9 g. of barbituric acid (30.4 mmoles) and 1.22 g. of sodium hydroxide (30.4 mmoles) in 100 ml. of water was added to a filtered solution of 10.0 g. of dibenziodolium sulphate (15.2 mmoles) in 600 ml of hot water. A precipitate of fine needle-shaped crystals was formed immediately after mixing. After drying 9.14 g. of almost

colourless product was isolated.

When iodide anion was added to the mother liquor there was only a faint turbidity. This indicated that the product was almost as insoluble in water as dibenziiodolium iodide.

The powdered compound when placed on a watch glass in a vacuum desiccator at 1-5 mm. visibly changed its colour to yellow in 2 minutes. The same change in colour could be effected by heating at 70° till constant weight was reached.

The infrared spectrum of the compound is reproduced in Fig. 5, and is discussed in Part III of Section 2.

The analyses of the product were carried out with material as it was isolated without further recrystallization because of its very low solubility. The results were in agreement with the structure of dibenziiodolium barbiturate monohydrate.

Analyses:

Calculated for $C_{16}H_{11}O_3N_2I$: I, 31.25.

Found : I, 31.29, 31.44.

Calculated for $C_{16}H_{11}O_3N_2I \cdot H_2O$: H_2O , 4.25.

Found : H_2O , 4.59.

At 220° the compound melted rapidly under decomposition, after its colour had started to darken at 195°.

Dibenziiodolium 5,5-dimethyl-2-phenyl-3-keto-1-cyclohexenolate (or 2-phenyldimedata)

2-Phenyldimedone and 2,2-diphenyldimedone were prepared according to the procedure of Beringer and co-workers (8) :

A solution of 4.2 g. of sodium (182 mg. atoms), 26.0 g. of dimedone

(180 mmoles), and 58.5 g. of diphenyliodonium chloride (186 mmoles) in 900 ml. of t-butyl alcohol was heated to reflux for 4 hours. From the reaction mixture were isolated 6.3 g. of 2,2-diphenyldimedone (21.5 mmoles) with m.p. 175.5-179° and 7.1 g. of 2-phenyldimedone (33.0 mmoles) with m.p. 192.5-195.5°, yields of 12% and 18% respectively.

A solution of 2.5 g. of 2-phenyldimedone (12.0 mmoles) and 0.48 g. of sodium hydroxide (12.0 mmoles) in 25 ml. of water was added to a hot filtered solution of 3.27 g. of 3.27 g. of dibenziodolium sulphate (5 mmoles) in 300 ml. of water. A bright yellow crystalline precipitate was formed immediately. The compound was very insoluble in cold or hot water, but soluble in methanol, ethanol, and dimethyl sulphoxide giving yellow solutions. When water was added slowly to a solution in one of the latter solvents its colour faded slowly at first, and later the solutions became colourless. When chloride or iodide ion was added to such a solution the corresponding dibenziodolium halides could be isolated with a yield of 92%.

The yellow compound was expected to be dibenziodolium 2-phenyldimedate. This was confirmed by analysis.

Analysis:

Calculated for $C_{26}H_{23}O_2I$: I, 25.67.

Found : I, 25.62 , 25.75.

The yield of the product was 3.76 g. (76%). The m.p. was 184-186° (dec.). The infrared spectrum is reproduced in Fig. 6 and is discussed in Part III of Section 2.

Dibenziodolium 2-naphthalenethiolate

A solution of 6.54 g. of dibenziodolium sulphate (100 mmoles) in 600 ml. of boiling water was added to 3 l. of water of 15°. The solution

was cooled to room temperature and filtered.

A solution of 4.0 g. of 2-naphthalenethiol (25.0mmoles) in a slight excess of sodium hydroxide solution was filtered and added directly to the dissolved dibenziodolium sulphate, avoiding contact of the thiolate with air. This was achieved by letting the stem of the funnel dip into the solution of the sulphate. Because the product of the reaction could not be recrystallized and the thiolate is very easily oxidized to 2,2'-dinaphthyl disulphide these precautions were taken.

When the solution of 2-naphthalenethiolate was added a brightly yellow flocculent precipitate was formed immediately. The mixture was filtered and the product was washed three times with distilled water.

The yield of dry dibenziodolium 2-naphthalenethiolate was 7.7 g. (17.6 mmoles) or 88%. The compound decomposed at 94.5°

Analysis:

Calculated for $C_{22}H_{15}SI$: S, 7.32 ; I, 28.95.

Found : S, 7.32 ; I, 28.54, 29.20.

The infrared spectrum of the compound is reproduced in Fig.7 in Part III of Section 2.

The decomposition of dibenziodolium 2-naphthalenethiolate in various solvents is described in Part V of Section 3.

SECTION 3

E X P E R I M E N T A L

P a r t V

Decomposition of Dibenziodolium 2-Naphthalenethiolate
in Various Solvents

Decomposition in cyclohexane

a. Dibenziodolium 2-naphthalenethiolate (20.0 g., 45.6 mmoles) was suspended in 500 ml. of cyclohexane (Fisher Certified Reagent) under a nitrogen atmosphere. The stirred suspension was heated to reflux for 258 hours and an almost clear yellow solution was obtained.

The cyclohexane was evaporated. When the yellow syrupy residue was cooled crystals were formed. Ten milliliters of 98% ethanol was added and the mixture was filtered. The crystalline material weighed 0.6 g. and was identified as 2,2'-dinaphthyl disulphide (1.9 mmole, yield 8.3%) by comparison of infrared spectra. When the compound was mixed with an authentic sample of the disulphide, which had been prepared by oxidation of the thiol and had m.p. 137.5-139° (reported (80) m.p. 139°), no depression was observed.

The ethanol was evaporated in vacuo from the filtrate and a residue weighing 18.85 g. was obtained. A vacuum distillation with the residue yielded 8.9 g. of pure 2-iodobiphenyl (32 mmoles) which was collected at 82-103° (0.20-0.25 mm.). It was identified by its infrared spectrum. Another fraction, which was collected at 103-131° (0.20-0.25 mm.) and weighed 0.5 g., consisted of a mixture of 2-iodobiphenyl and a product

of which the bulk was collected at 131-135° (0.20 mm.). This was a very viscous liquid weighing 6.3 g., which solidified after a short time. It contained only a trace of iodine and its infrared spectrum showed a very weak absorption at 685 cm^{-1} , caused by the presence of 2-iodobiphenyl. The distillation residue was fairly large and weighed 3 g.

The unknown product was recrystallized from 110 ml. of methanol-water (10:1). Needle-shaped crystals were obtained with m.p. 44.5-47°. To prepare an analytical sample part of this material was recrystallized from ethanol. This raised the m.p. to 47°. The compound was expected to be cyclohexyl 2-naphthyl sulphide and this was confirmed by analysis, infrared spectrum and derivatives that were prepared. The infrared spectrum has been reproduced in Fig. 8 and is discussed in Part IV of Section 2.

Analysis:

Calculated for $\text{C}_{16}\text{H}_{18}\text{S}$: C, 79.28 ; H, 7.49 ; S, 13.23.

Found : C, 79.46 ; H, 7.61 ; S, 13.28.

This sulphide could be oxidized with peracetic acid to cyclohexyl 2-naphthyl sulphone, with m.p. 98°.

Analysis:

Calculated for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}$: C, 70.04 ; H, 6.61 ; S, 11.69.

Found : C, 70.08 ; H, 6.70 ; S, 11.59.

In this experiment 6.3 g. of cyclohexyl 2-naphthyl sulphide (26 mmoles) was isolated; that is a yield of 57%.

If it is assumed that the middle fraction contains equal parts of the sulphide and of 2-iodobiphenyl the total yield of the latter compound is 9.15 g. or 72% .

In another similar experiment the yields of 2-iodobiphenyl and cyclohexyl 2-naphthyl sulphide were 72% and 53% respectively.

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b. Before it was found that cyclohexyl 2-naphthyl sulphide could most satisfactorily be isolated by means of a vacuum distillation it was attempted to separate 2-iodobiphenyl from the sulphide by chromatography on alumina. The elution was started with n-hexane but no separation was obtained with this solvent.

A better method for the isolation of the sulphide was a steam distillation of the oily decomposition product. After prolonged distillation the residue was almost pure cyclohexyl 2-naphthyl sulphide. This method was lengthy, however, and the distillation in vacuo was preferred.

c. Preparation of the sulphilimine of cyclohexyl 2-naphthyl sulphide was carried out by the following procedure (41c, 53):

A solution of 3.4 g. of chloramin T (12.0 mmoles) in 50% ethanol was added to a solution of 2.0 g. of cyclohexyl 2-naphthyl sulphide (8.0 mmoles) in 5 ml. of 98% ethanol. The mixture was heated for 50 minutes at 80° and left to cool overnight to room temperature. Prolonged heating of the solution of the sulphilimine, also during recrystallization, was avoided (81).

During the period of cooling no crystallization took place, but after the Erlenmeyer flask that contained the solution had been scratched with a stirring rod an oil was formed promptly which solidified later. After recrystallization from ethanol 2.13 g. of the sulphilimine (yield 65%) was obtained with m.p. 136-137°. A mixture of toluene and cyclohexane used by Vecera and Petranek (82) for the crystallization of many sulphilimines proved to be not very satisfactory when it was tried: the m.p. decreased to 135-137°. After an additional crystallization in ethanol an analytical sample was obtained, m.p. 136-137°.

Analysis:

Calculated for $C_{23}H_{25}O_2NS_2$: C, 67.12 ; H, 6.12 ; N, 3.40 ; S, 15.58.

Found : C, 67.15 ; H, 6.09 ; N, 3.51 ; S, 15.67.

The infrared spectrum of cyclohexyl 2-naphthyl sulphilimine is reproduced in Fig.9 and is discussed in Part IV of Section 2. It was compared with the spectrum of the sulphilimine of diphenylsulphide. This sulphilimine was prepared and had a m.p. 109-110°. Reported m.p. 108-110° (83).

Decomposition in carbon tetrachloride

Dibenziodolium 2-naphthalenethiolate (2.6 g., 6 mmoles) was suspended in 70 ml. of carbon tetrachloride in a nitrogen atmosphere. The solvent was "Mallinckrodt Analytical Reagent, low in sulphur". When shaken with an aqueous solution of silver nitrate no turbidity appeared.

The suspension was stirred for 150 minutes in the sunlight and for 15 hours in ultraviolet light (Hanovia lamp, Type 30600). Room temperature was maintained all the time by cooling with an air stream. The reaction mixture was filtered and after crystallization of the precipitate from water 0.23 g. of dibenziodolium chloride (0.7 mmole) was obtained. This was a yield of 12%. The chloride was identified by analysis and comparison with an authentic sample.

After the solvent had been evaporated from the filtrate there was a brown syrupy residue. Part of it solidified when it was cooled and some ethanol was added. Most of the residue dissolved in the alcohol. By filtration 0.21 g. of crude 2,2'-dinaphthyl disulphide was obtained, which was recrystallized from ethanol giving 0.17 g. of pure disulphide (0.5 mmoles) , or a yield of 18%. It was identified by comparison with

an authentic sample.

The ethanolic filtrate was concentrated to a small volume, ether was added and the solution was dried with anhydrous magnesium sulphate. After evaporation of the ether 1.64 g. of a brown oil was isolated. The oil had a strong acidic odour, very much like hydrochloric acid, and especially well noticeable after it had been stored in a closed container for some time. Blue litmus paper turned red when held over the vial containing this oil. In the oil 2,2'-dinaphthyl disulphide was formed on standing. Part of the oil weighing 0.6 g. was subjected to partition chromatography on alumina (Fisher 20-200 mesh).

Successively n-hexane, benzene, diethyl ether, and methanol were used in the elution. More than half of the material (0.36 g.) was collected in the first two n-hexane fractions. The infrared spectrum of this material was identical with the spectrum of 2-chloro-2'-iodobiphenyl, of which an authentic sample had been prepared (see Part I of Section 3), except for a very small impurity. Recrystallization of the slightly impure product from ethanol and aqueous methanol raised the m.p. from 49-50° to 57-58.5°. Mixed with authentic 2-chloro-2'-iodobiphenyl, which melted at 62.0-63.5°, the m.p. was 57.5-61.5°. On the basis of the quantity of 2-chloro-2'-iodobiphenyl that was isolated from 0.6 g. of the oily decomposition product the yield of this disubstituted biphenyl was calculated as 52%.

The material collected in the following fractions in the chromatographic separation could not be identified.

Decomposition in tetrahydrofuran

Tetrahydrofuran (Eastman Kodak Co., White Label) was distilled

to free it from hydroquinone and passed through a column of adsorption alumina (Fisher 20-200 mesh) to remove peroxide (84). It was collected and stored under nitrogen and always tested for the presence of peroxide immediately before use.

a. Dibenziodolium 2-naphthalenethiolate (7.2 g., 16.4 mmoles) was shaken at room temperature in 125 ml. of tetrahydrofuran in a nitrogen atmosphere. It decomposed and after 24 hours the yellow solution was filtered and concentrated in vacuo. Ethanol was added to the residue and the alcoholic solution was filtered. The yield of 2,2'-dinaphthyl disulphide was 0.33 g. (1.0 mmole) or 12.5%.

The filtrate was concentrated in vacuo and 6.8 g. of an oily residue was isolated. The infrared spectrum showed that large quantities of 2-iodobiphenyl were present in this material, but the aliphatic C-H stretching absorptions and a strong absorption at 1050 cm^{-1} indicated that another, at least partly aliphatic, compound was present.

In the following attempts to isolate this material the absorption at 1050 cm^{-1} was used as a guide. A steam distillation was carried out with the oily residue. When 6 l. of distillate had been collected it was extracted with ether. The ethereal extract yielded 2-iodobiphenyl, which was still slightly contaminated. The residue of the steam distillation was dissolved in ether. The ethereal solution was dried with anhydrous magnesium sulphate. After evaporation of the ether an oil was obtained, which still contained some 2-iodobiphenyl. Chromatography of this material on alumina (Fisher 20-200 mesh) and elution with n-hexane - benzene (1:1) afforded an oil which contained no 2-iodobiphenyl, as was indicated by its infrared spectrum.

This product was thought to be 2-naphthyl tetrahydro-2-furyl

7
sulphide. The infrared spectrum of this compound has been reproduced in Fig.10, and is discussed in Part IV of Section 2.

Analysis:

Calculated for $C_{14}H_{14}OS$: S, 13.92.

Found : S, 13.60

This sulphide was not stable. 2,2'-Dinaphthyl disulphide was formed when it was left standing in a closed container .

b. To determine the yield of the products a decomposition was carried out on a larger scale.

Dibenziodolium 2-naphthalenethiolate (20.0 g., 45.6 mmoles) decomposed in 15 minutes when it was stirred at 43° in 425 ml. of peroxide-free tetrahydrofuran exposed to sunlight and under a nitrogen atmosphere.

The yield of 2,2'-dinaphthyl disulphide, which was isolated as in the preceding experiment, was 0.4 g. (1.2 mmole) or 5.5%.

No steam distillation was used in this experiment but twice repeated chromatography on alumina with n-hexane and benzene gave a good separation. The yield of pure 2-iodobiphenyl was 10.85 g. (39 mmoles) or 85%. The only other product isolated was a yellow oil of which the infrared spectrum was identical with that taken of 2-naphthyl tetrahydro-2-furyl sulphide prepared in the preceding experiment. The yield was 8.1 g. (35 mmoles) or 77%.

Several attempts to separate 2-iodobiphenyl from the other product by fractional distillation in vacuo were unsuccessful. Even when the distillation of 2-iodobiphenyl was carried out at 0.05-0.10 mm. decomposition of the residue occurred at a bath temperature of 65°, and 2,2'-dinaphthyl disulphide was formed. All attempts to prepare a derivative

of the isolated sulphide were unsuccessful.

Attempts to Decompose Dibenziodolium p-Toluenesulphonate
in Cyclohexane and Carbon Tetrachloride

Decomposition in cyclohexane (attempted)

a. A suspension of 2.087 g. of dibenziodolium p-toluenesulphonate in 100 ml. of cyclohexane (Fisher Certified Reagent) was shaken at room temperature in a nitrogen atmosphere and was exposed to ultraviolet light (Hanovia lamp, Type 30600). After 186 hours of irradiation the suspension was filtered and 2.021 g. of p-toluenesulphonate was recovered.

The cyclohexane was evaporated. The residue weighed 10.9 mg. By means of its infrared spectrum it was identified as silicone grease. No decomposition of the salt took place apparently.

b. A suspension of 0.340 g. of dibenziodolium p-toluenesulphonate in 75 ml. of cyclohexane (Fisher Certified Reagent) was heated to reflux for 48 hours after which 0.301 g. of dibenziodolium salt was recovered. There was no residue after evaporation of the solvent.

Decomposition in carbon tetrachloride (attempted)

A suspension of 2.548 g. of dibenziodolium p-toluenesulphonate in 70 ml. of carbon tetrachloride (Mallinckrodt Analytical Reagent, low in sulphur) was stirred in a nitrogen atmosphere at room temperature exposed to ultraviolet light (Hanovia lamp, Type 30600). After 48 hours

of irradiation the suspension was filtered. The recovered p-toluene-sulphonate was dried in a vacuum ; it weighed 2.478 g. and contained no chloride ion. The solvent was evaporated from the filtrate. The very small residue weighed 2 mg. and consisted of silicone grease as was indicated by the infrared spectrum.

No decomposition of the salt had taken place.

No chloride ion could be detected immediately after 100 ml. of the same carbon tetrachloride as was used before had been shaken for 72 hours in ultraviolet light at room temperature and in a nitrogen atmosphere. When shaken with an aqueous solution of silver nitrate there was no turbidity in the aqueous layer.

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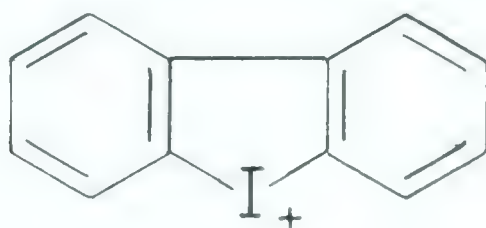
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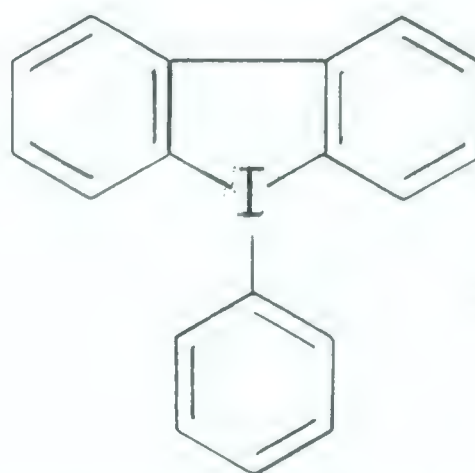
APPENDIX

NOMENCLATURE

For two types of iodine-containing compounds, I and II, which are mentioned in this thesis, the names usually encountered in the literature seemed unsatisfactory and incompatible with the "IUPAC 1957 Rules" for the nomenclature of hydrocarbons and fundamental heterocyclic systems (85).



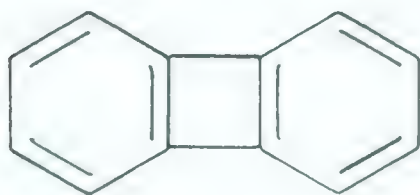
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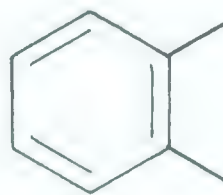
II

For cation I the names biphenyleneiodonium, diphenyleneiodonium, and 2,2'-biphenyliodonium have been used (7, 28, 31).

The name biphenylene has been reserved for compound III (Rule A-21.2).



III

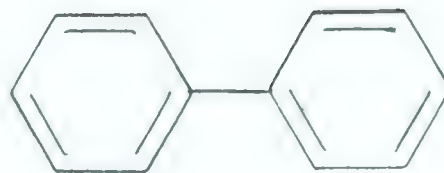


IV

According to Rule A-11.6 the name phenylene may be used for the

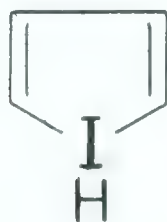
bivalent group IV (o-phenylene shown).

Cation I is rather a derivative of V, biphenyl according to Rule A-52.4 , than of IV, but it is incorrect to use the name 2,2'-biphenyl-ylidonium, attaching the suffix -yl to a name ending with -yl.

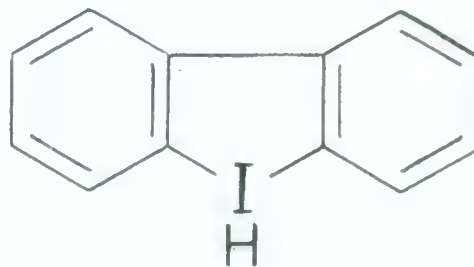


V

Application of Rule B-1 for naming heterocyclic compounds seems to the present author a straightforward method which gives the name iodole for the unknown parent compound VI. Compound II would be a derivative of dibenziiodole, VII, also unknown.

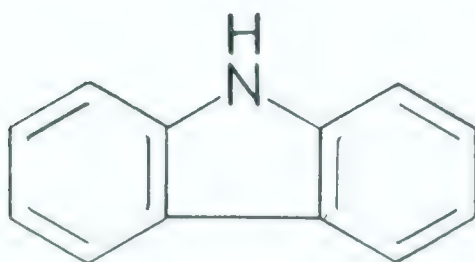


VI

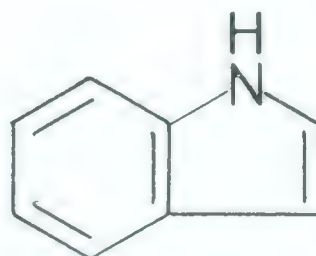


VII

Chemical Abstracts uses the name 5H-dibenziiodole for VII, but the indicated hydrogen is not consistent with the official names carbazole and indole for VIII and IX, where no hydrogen is indicated (Rule B-2.11).



VIII



IX

Once dibenziiodole is accepted for VII, the name dibenziiodolium for cation I follows automatically.

Adoption of this nomenclature is also necessary because several iodonium compounds have been prepared in which the iodine is part of a six-, seven-, or eight-membered ring (67, 86). Their names can be derived from respectively iodininium, iodepinium, and iodocinium.

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